

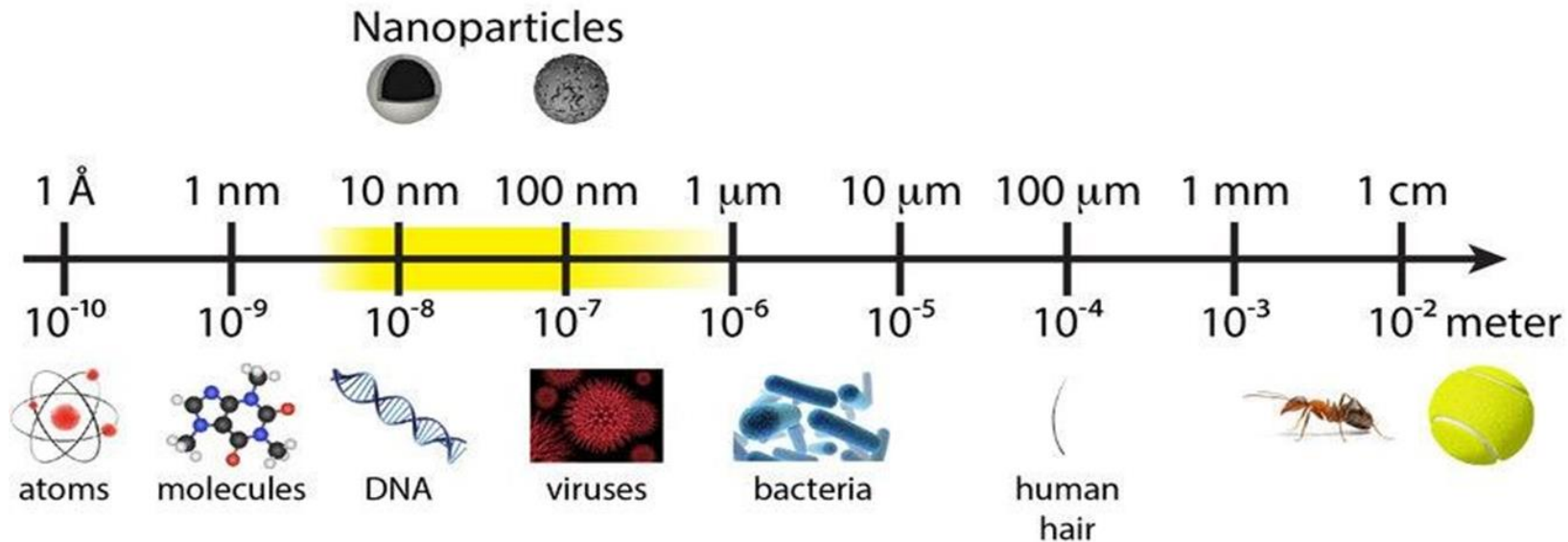
# Is this Nano?

Nanotechnology is a “system of innovative methods to control and manipulate matter at near-atomic scale to produce new materials, structures, and devices”.



## Nanomaterials (NMs)

Materials in the range of 100 nm are considered to be nanoparticles. They exhibit a wide range of properties, including optical, electrical, catalytic, magnetic, and biological activity.



# Metal nanoparticles

Metal nanoparticles are tiny particles of metals that have dimensions typically in the range of 1 to 100 nanometers. At this scale, materials exhibit unique physical, chemical, and optical properties that differ significantly from their bulk counterparts due to quantum effects and a high surface area-to-volume ratio. Here are key features and details about metal nanoparticles:

## Characteristics of Metal Nanoparticles

### 1. Size and Shape:

1. Their nanoscale size gives them distinct properties.
2. They can have various shapes like spheres, rods, cubes, or plates, which influence their behavior and applications.

### 2. High Surface Area:

1. Due to their small size, metal nanoparticles have a high ratio of surface atoms compared to bulk materials, enhancing their reactivity.

### 3. Optical Properties:

1. Metal nanoparticles exhibit localized surface plasmon resonance (LSPR), where electrons resonate with light at specific wavelengths, leading to vibrant colors (e.g., gold nanoparticles appearing red or purple).

### 4. Quantum Effects:

1. The electronic properties of metal nanoparticles are size-dependent, making them useful in catalysis, electronics, and quantum dot technologies.

## Common Types of Metal Nanoparticles

- Gold (Au) Nanoparticles:** Widely used in medical imaging, drug delivery, and as catalysts.
- Silver (Ag) Nanoparticles:** Known for their antimicrobial properties, used in coatings and textiles.
- Platinum (Pt) Nanoparticles:** Used in fuel cells and as catalysts in chemical reactions.
- Iron (Fe) Nanoparticles:** Often employed in environmental remediation and magnetic applications.

## Synthesis Methods

- Physical Methods:** Laser ablation, evaporation-condensation techniques.
- Chemical Methods:** Reduction of metal salts in solution using reducing agents like citrate or borohydride.
- Biological Methods:** Utilizing plant extracts, bacteria, or fungi for eco-friendly synthesis.

## Applications

### 1.Catalysis:

1. Metal nanoparticles accelerate chemical reactions due to their high reactivity and surface area.

### 2.Biomedical Uses:

1. Targeted drug delivery, cancer treatment, imaging, and biosensors.

### 3.Environmental Remediation:

1. Removal of pollutants or heavy metals from water and soil.

### 4.Electronics:

1. Used in conductive inks, circuits, and memory devices.

### 5.Optics and Photonics:

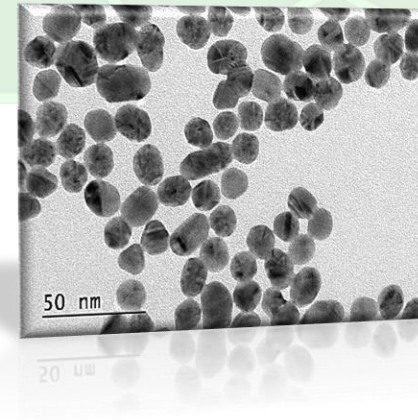
1. Enhancement of optical devices and sensors using their plasmonic properties.

## Safety and Environmental Considerations

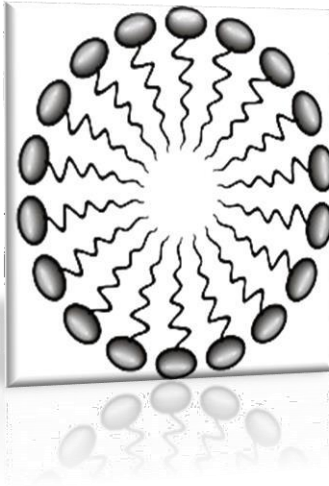
While metal nanoparticles have exciting applications, their potential toxicity and environmental impact are subjects of ongoing research. Careful assessment and regulation are essential to balance benefits with risks.

Metal nanoparticles are a frontier of nanotechnology with immense potential across industries, driven by their unique properties at the nanoscale.

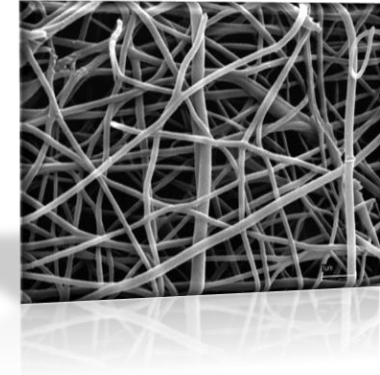
Nano-objects  
Nano-particles



Micelle



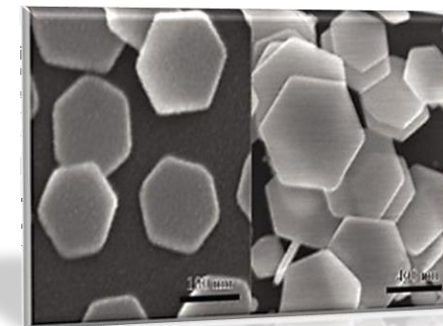
Nanofiber



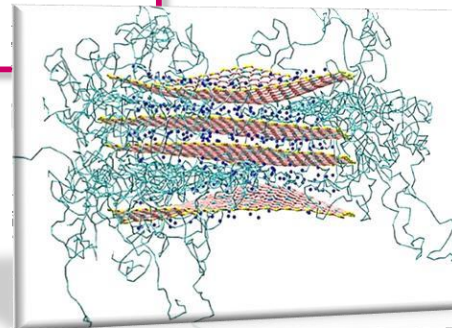
**Nanomaterials  
(NMs)**

Nanoformulations

Nanoplate

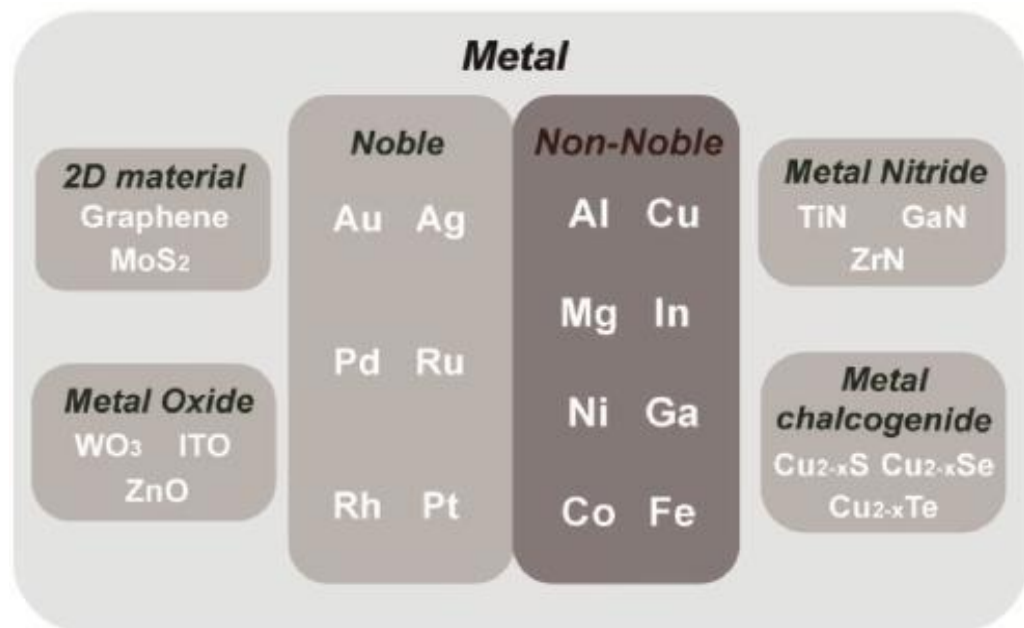


*Nanocomposite*



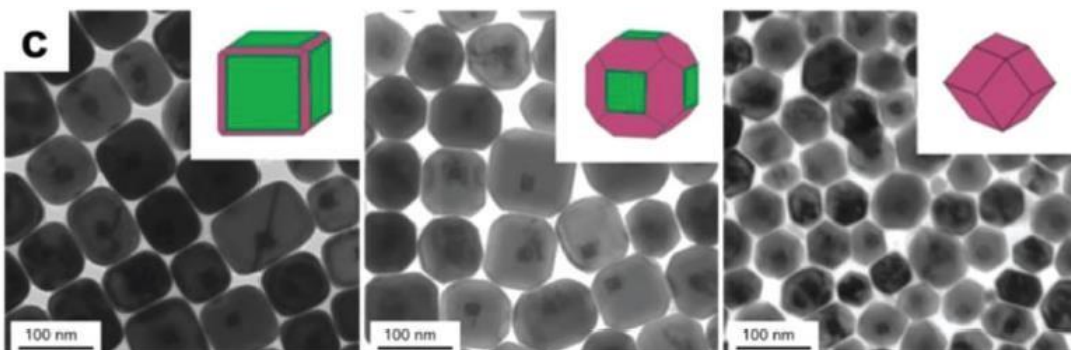
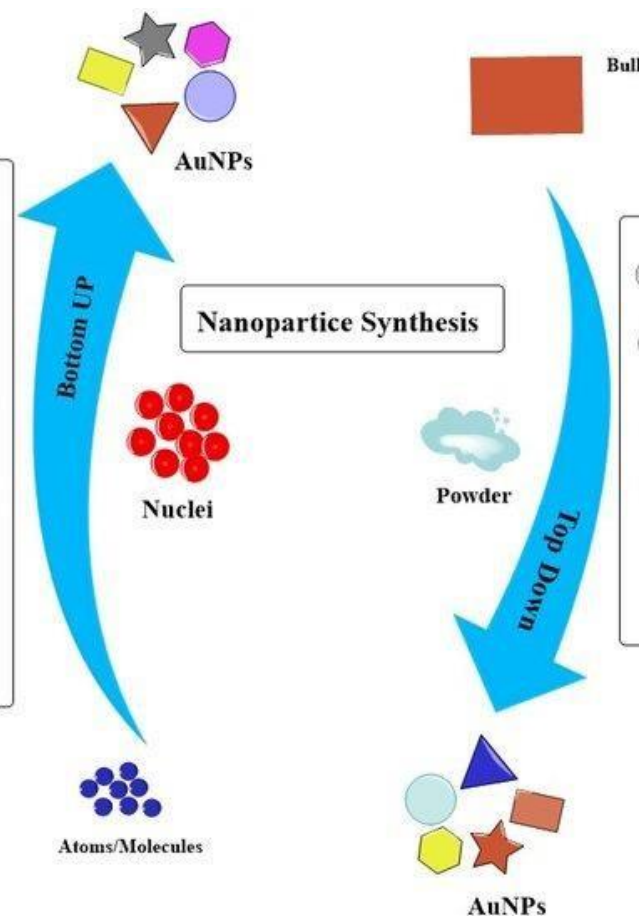


# Metal based Nanoparticles

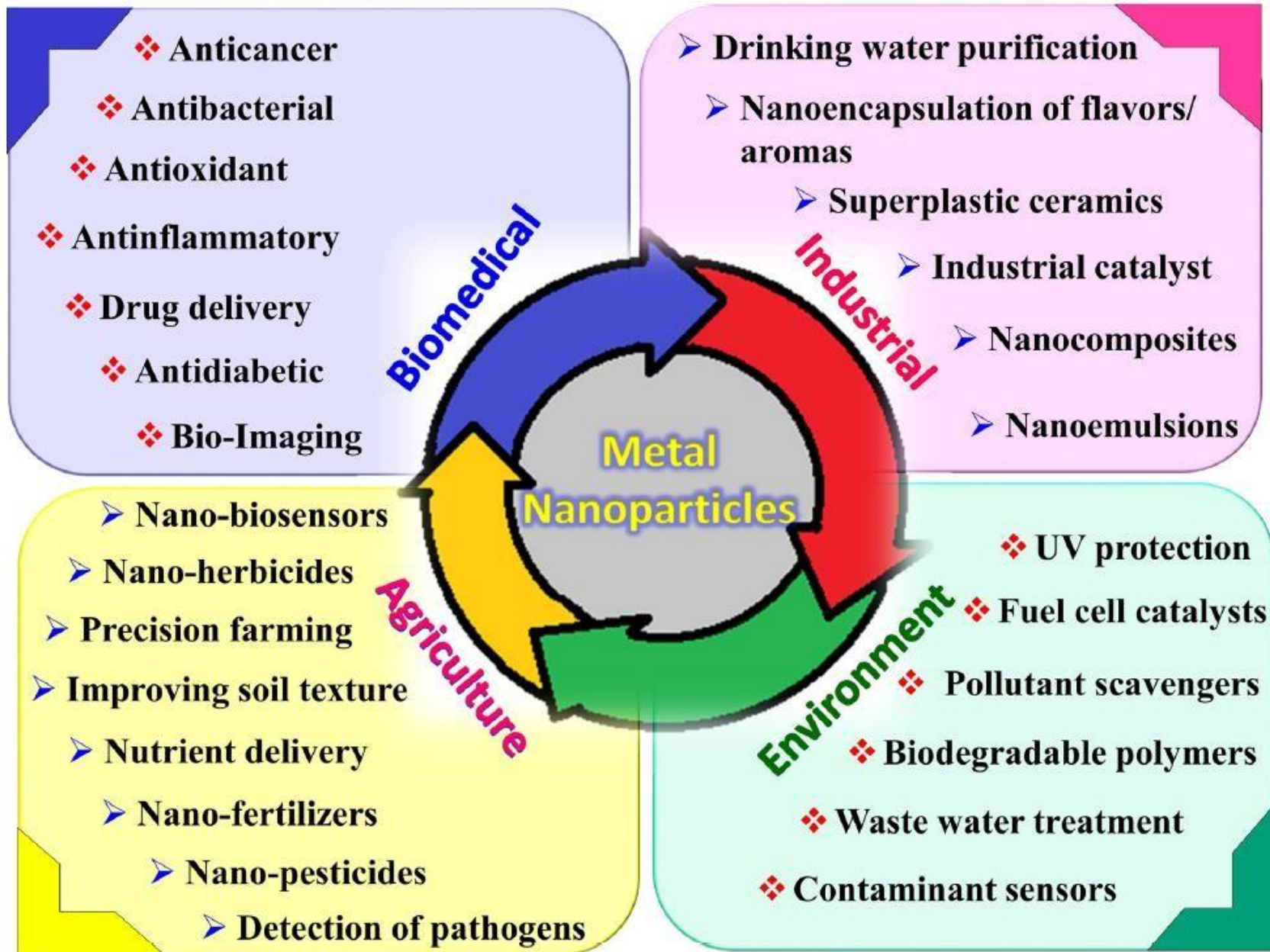


- Atomic/ Molecular Condensation
- Vapour Deposition
- Sol-gel Process
- Spray Pyrolysis
- Chemical/Electrochemical Deposition
- Aerosol Process
- Bioreduction

- Sputtering
- Chemical etching
- Thermal/Laser ablation
- Mechanical/Ball missing
- Explosion Process



# Metal Nanoparticles application fields

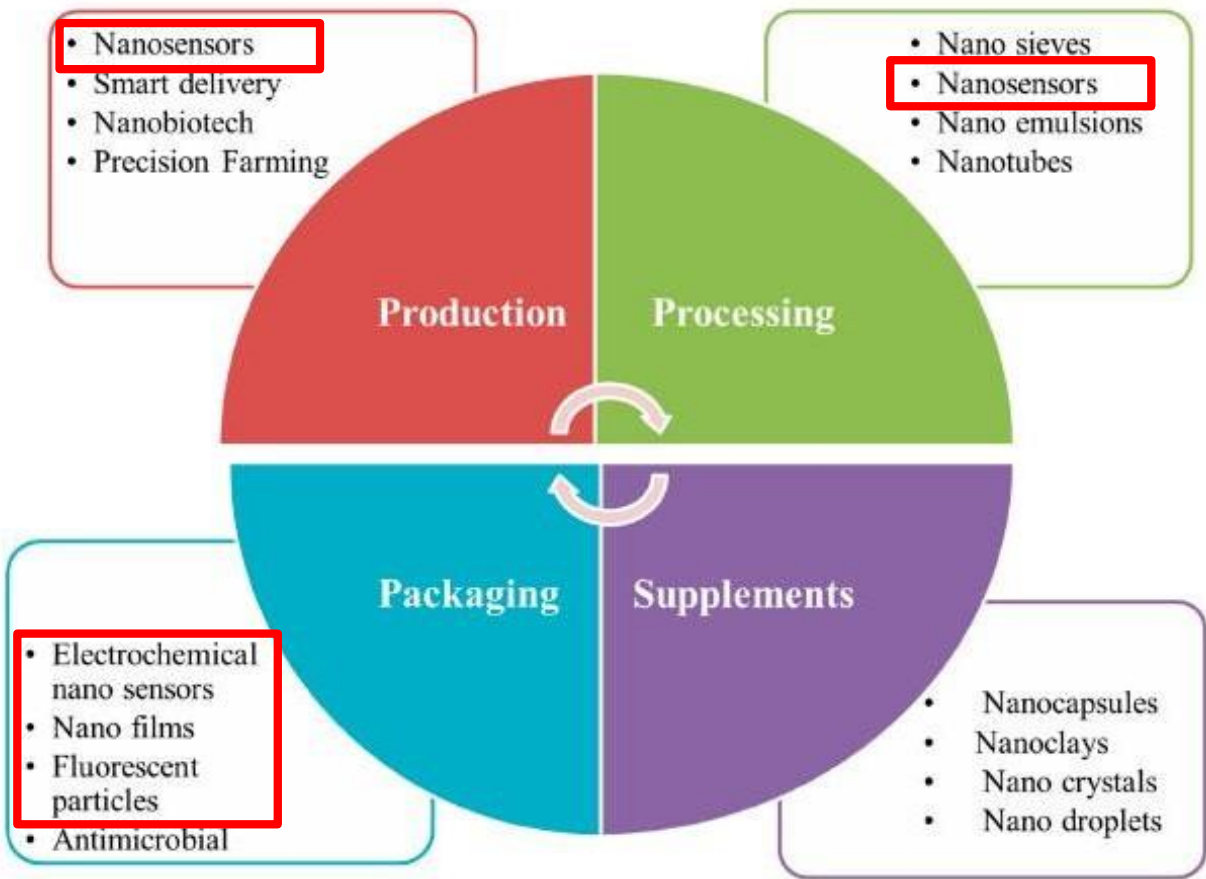




Review

## An Overview of the Applications of Nanomaterials and Nanodevices in the Food Industry

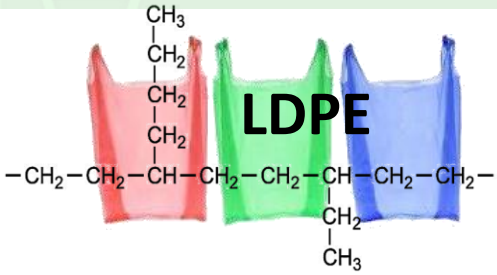
Mehwish Shafiq <sup>1</sup>, Sumaira Anjum <sup>1,\*</sup>, Christophe Hano <sup>2</sup>, Iram Anjum <sup>1</sup> and Bilal Haider Abbasi <sup>3</sup>



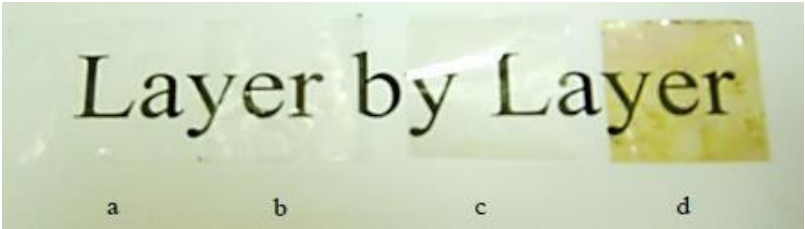
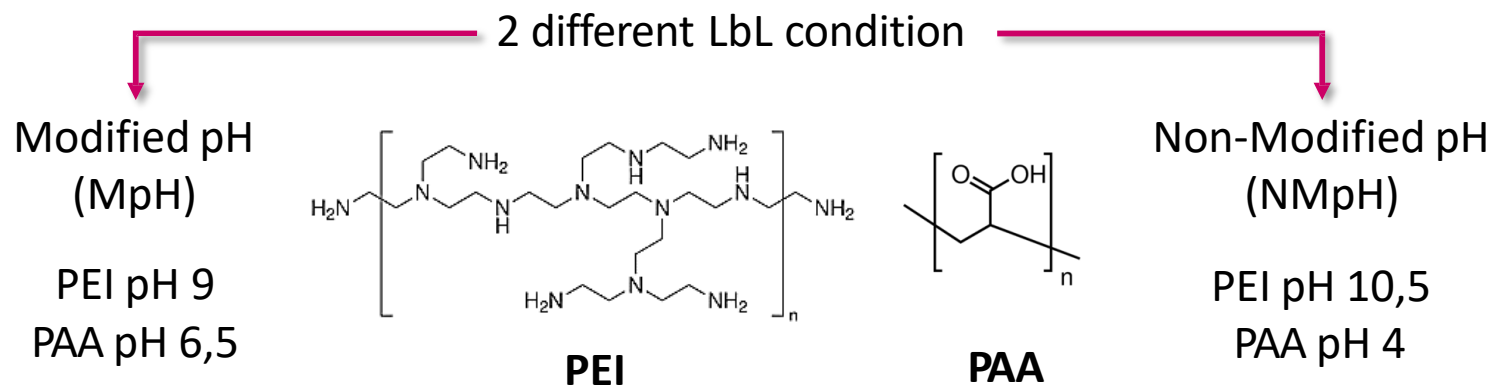
Nanomaterials	Type of Nanomaterials	Applications in Food Industry
Nanoparticles	Ag, ZnO, Mg, SiO <sub>2</sub>	Food packaging, oxidation of contaminant, anti-bacterial
Nanosieves	Specific nanoparticles	Removal of pathogens or contaminants
Nanocapsules	Bioactive compounds	Increased efficacy and water solubility, local and controlled release
Nano-emulsions	Tweens or spans; gum arabica or modified starch, soy, caseinate	Food encapsulation, food processing, antimicrobial and storage, stability, colorant
Nanospheres	Starch nanosphere	Food encapsulation, synthetic adhesives
Nanosensors	Aptasensors	Detection of micro-organisms, food deterioration control
Nanocochleates	Coiled Nanoparticles	Enhanced nutritional value of food, antioxidant, food protection and stability
Nanocomposite	Fe-Cr/Al <sub>2</sub> O <sub>3</sub> Ni/Al <sub>2</sub> O <sub>3</sub>	Enhanced shelf life of food, food protection and food packaging
Nanomicelles	Aquanova, novasol	Liquid carrier, enhanced solubility



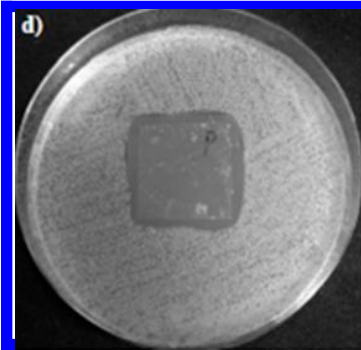
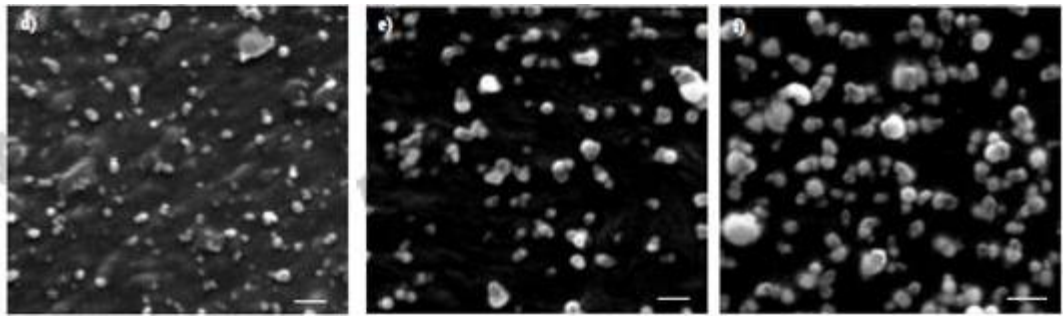
# Nanoparticles application in food technology



Commercial low-density polyethylene (LDPE) films coated using a layer-by-layer (LbL) technique by alternating the deposition of polyethyleneimine (PEI), poly(acrylic acid) polymer (PAA) solutions and antimicrobial silver nanoparticles (Ag).



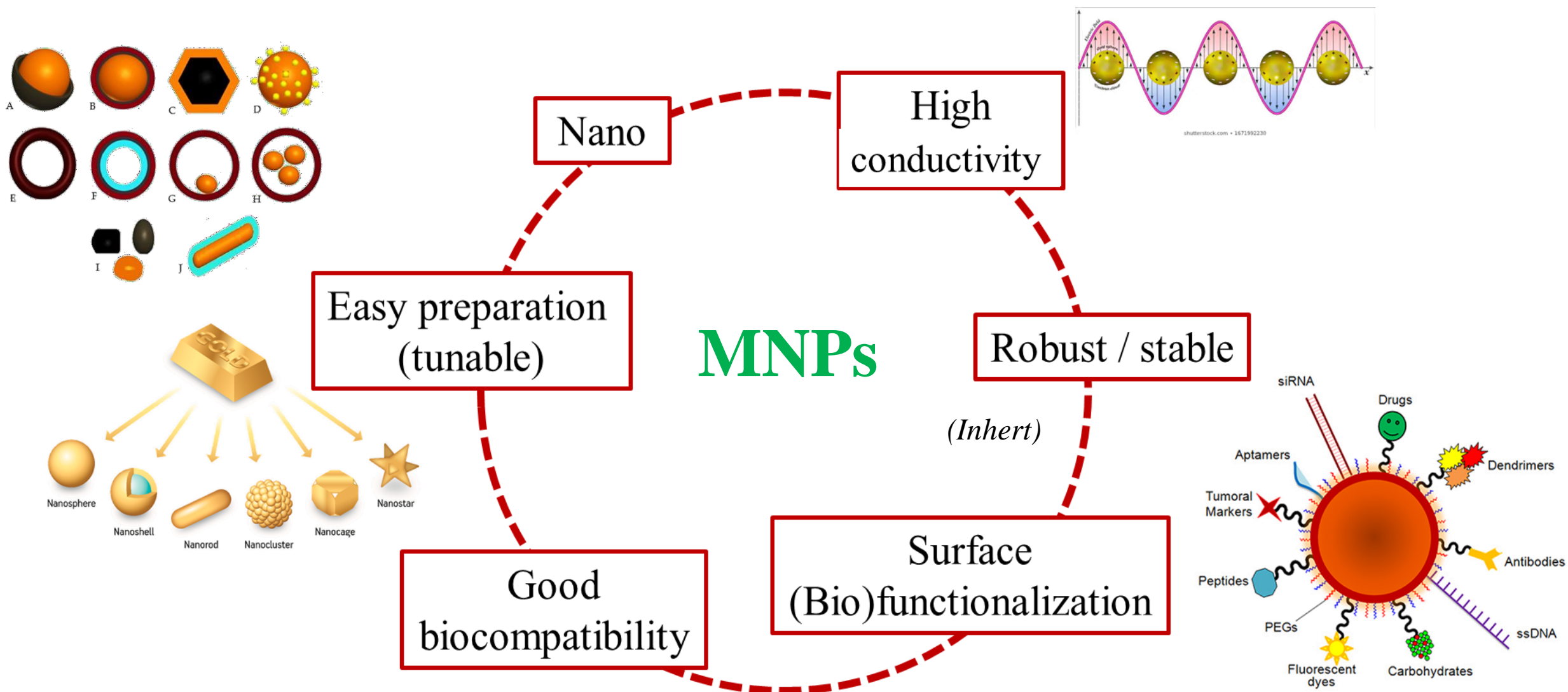
The colour changes of a) LDPE films and b) LDPE LbL coated (3 coatings) films without Ag and c) AgNPs presence on LDPE LbL coated (3 coatings) films immersed in 0,5% AgNO<sub>3</sub>, or d) AgNPs presence on LDPE LbL coated with (3 coatings) film immersed in 5% AgNO<sub>3</sub> and UV/ozone treated for 20 min.



Film	Inibition zone (mm <sup>2</sup> )	
	<i>S. aureus</i>	<i>P. fluorescens</i>
LPDE films	0.00	0.00
LPDE + PEI/PAA (MpH)	350.4 ± 13.30	694.8 ± 19.15
LPDE + PEI/PAA (NMpH)	460.0 ± 25.41	737.0 ± 15.08

(d) LbL coated (3 coating) immersed in 0,5% AgNO<sub>3</sub>, (e) LbL coated (3 coatings) immersed in 2% AgNO<sub>3</sub>; and (f) LbL coated (3 coatings) immersed in 5% AgNO<sub>3</sub>. Scale bar = 500nm

# Advantages of metal nanoparticles for analytical purposes





**Localized Surface Plasmon Resonance (LSPR)** is a phenomenon where conduction electrons on the surface of metal nanoparticles oscillate collectively in resonance with the electromagnetic field of incident light. This effect occurs in nanoparticles of certain metals, such as gold (Au), silver (Ag), and copper (Cu), when they are illuminated by light of specific wavelengths.

## **Key Features of LSPR**

### **1. Localized Nature:**

The oscillation of electrons is confined to the surface of the nanoparticles due to their small size and interaction with light.

### **2. Size and Shape Dependence:**

The resonance wavelength of LSPR is highly dependent on the size, shape, and composition of the nanoparticles. For example:

- a. Spherical gold nanoparticles typically resonate with red or green light.
- b. Rod-shaped particles may shift the resonance to infrared or other regions.

### **3. Material-Specific Behavior:**

Noble metals like gold and silver exhibit strong LSPR because they have free electrons that can oscillate easily under an electromagnetic field.

### **4. Sensitivity to Environment:**

The LSPR frequency is influenced by the surrounding medium, including the refractive index. This property makes LSPR highly sensitive for detecting changes in the local environment.

## **Mechanism of LSPR**

### **1.Interaction with Light:**

When light strikes a metal nanoparticle, it causes the free conduction electrons (from the metal's conduction band) to oscillate collectively at a specific frequency.

### **2.Resonance:**

If the frequency of light matches the natural oscillation frequency of the electrons, resonance occurs. This amplifies the oscillation and enhances the electromagnetic field around the nanoparticle.

### **3.Energy Dissipation:**

The resonance leads to strong absorption (not as electronic transitions of molecules!) and scattering of light. The absorbed energy can dissipate as heat or radiate as scattered light.

## **Applications of LSPR**

### **1.Sensing:**

**Biosensors:** Changes in the LSPR frequency can detect biomolecules binding to a nanoparticle's surface.

**Environmental Monitoring:** Detecting pollutants or chemical changes in a medium.

### **2.Medical Imaging:**

Enhanced contrast in imaging techniques due to strong light scattering by nanoparticles.

### **3.Photothermal Therapy:**

Gold nanoparticles can absorb light at their LSPR frequency, converting it into heat for targeted cancer treatments.

### **4.Catalysis:**

Enhanced catalytic activity due to the intense localized electromagnetic field at the nanoparticle surface.

### **5.Optoelectronic Devices:**

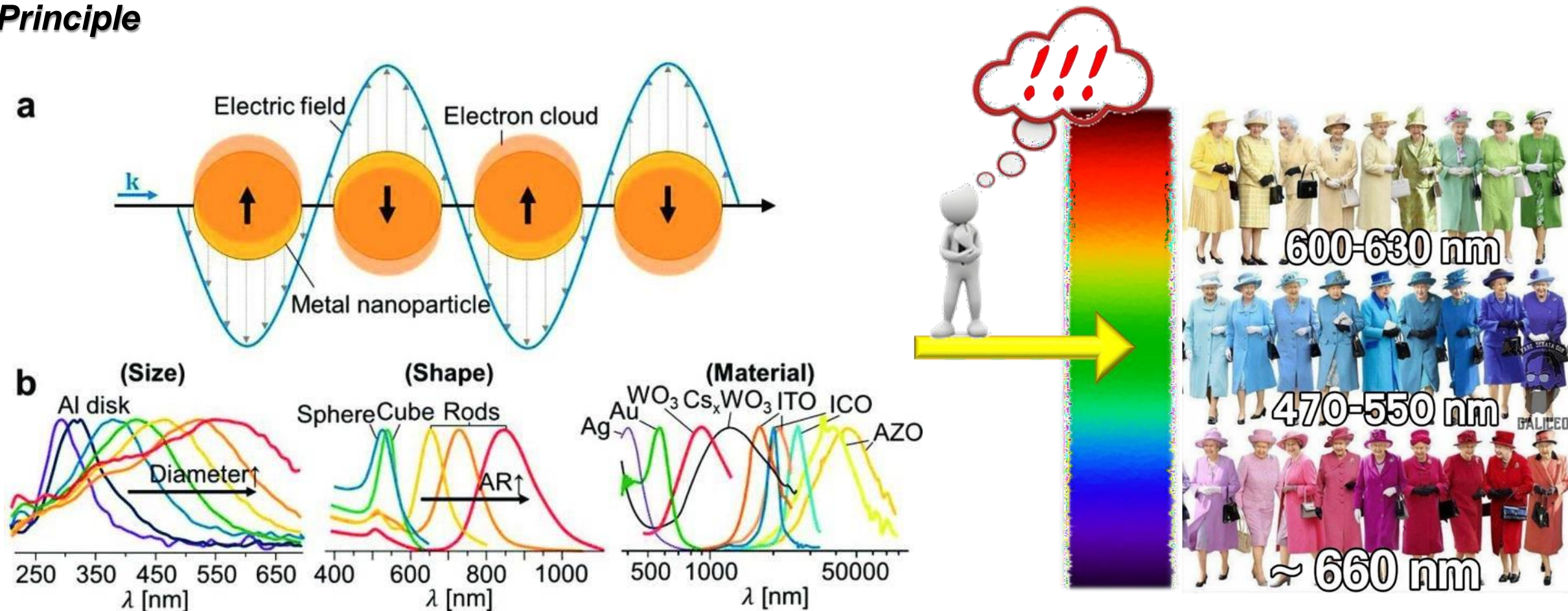
LSPR enhances light-matter interaction, improving the efficiency of devices like solar cells and LEDs.

## **Advantages of LSPR**

- High sensitivity to small environmental changes.
- Tunable properties by modifying the nanoparticle size, shape, and material.
- Versatility in biological, chemical, and physical applications.

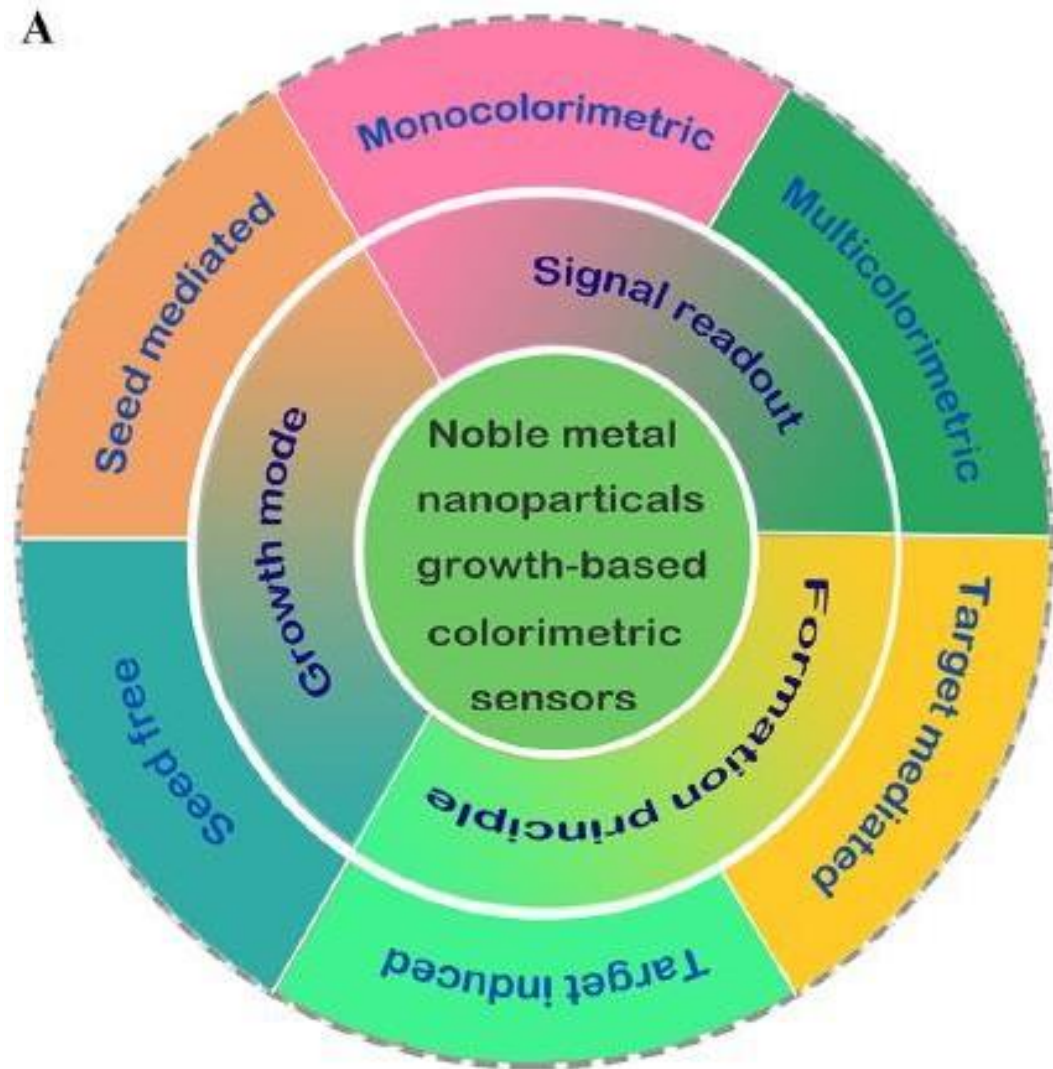
# Localized Surface Plasmon Resonance (LSPR)

## Principle

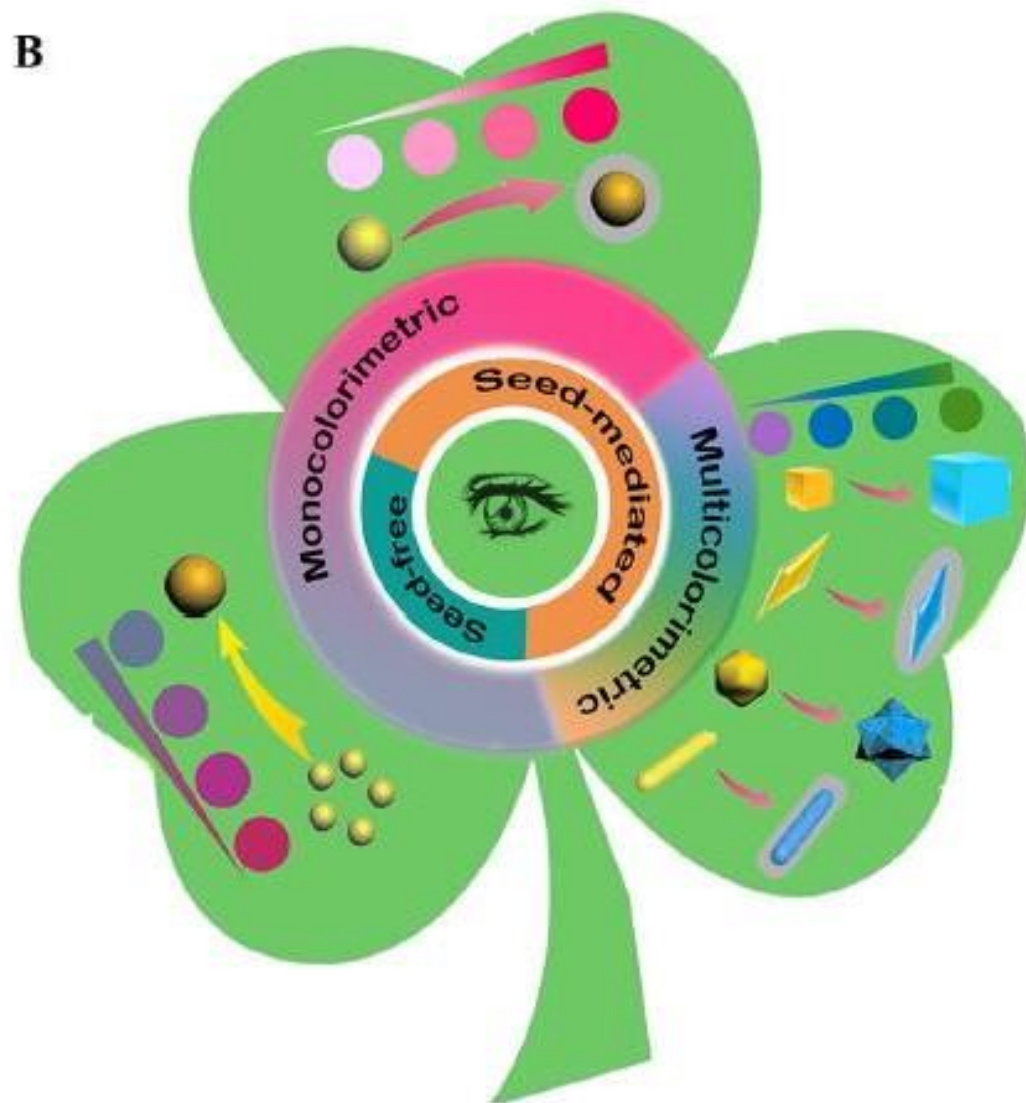


GÉRARD, Davy; GRAY, Stephen K. Aluminium plasmonics. *Journal of Physics D: Applied Physics*, 2014, 48.18: 184001.  
CHEN, Huanjun, et al. Shape-and size-dependent refractive index sensitivity of gold nanoparticles. *Langmuir*, 2008, 24.10: 5233-5237.  
LOUNIS, Sebastien D., et al. Defect chemistry and plasmon physics of colloidal metal oxide nanocrystals. *The journal of physical chemistry letters*, 2014, 5.9: 1564-1574.

A

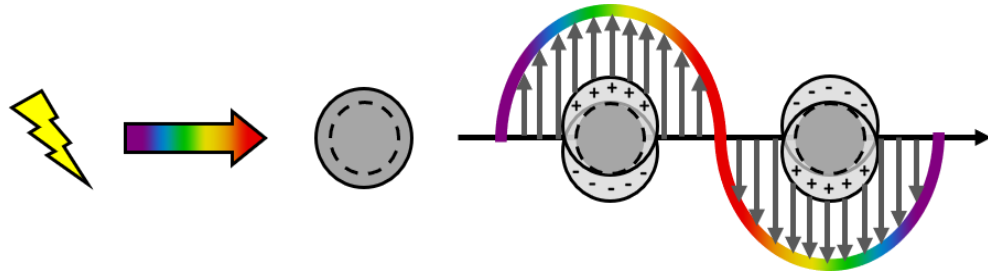


B

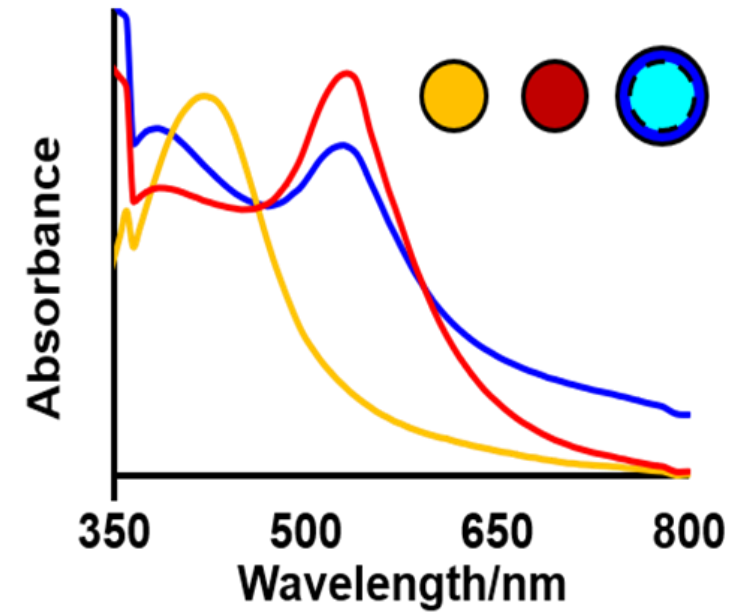
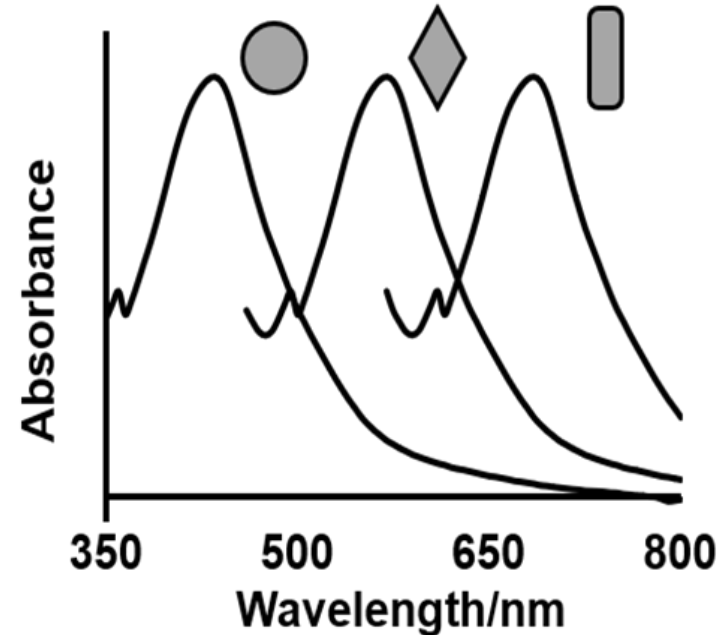
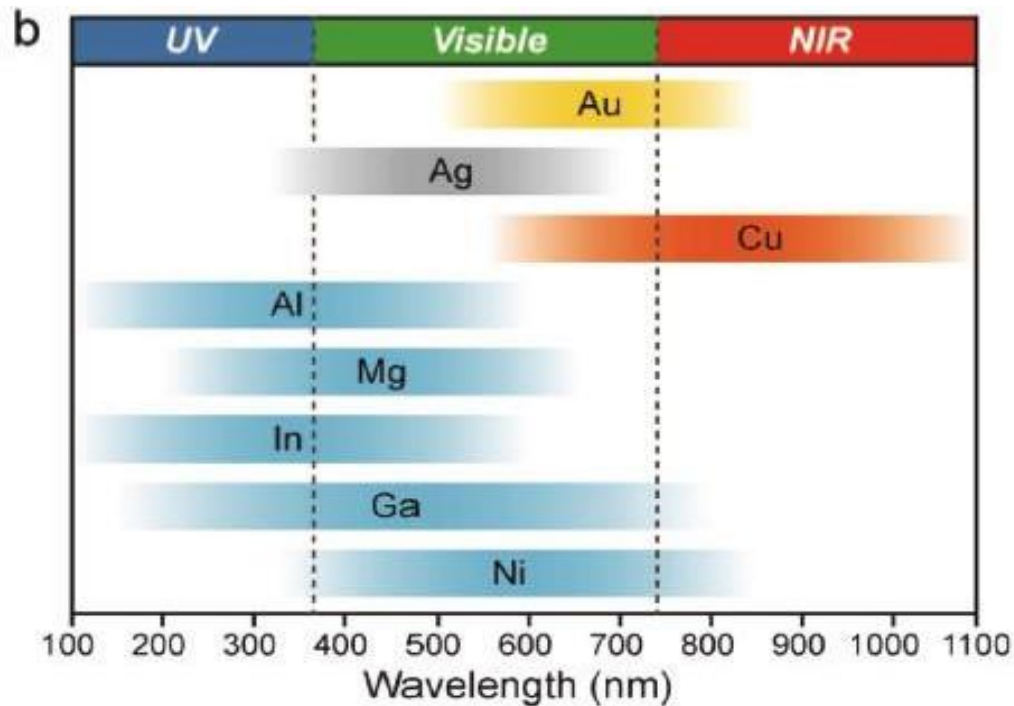




# Metal nanoparticles optical key features



## Localized Surface Plasmon Resonance





## Colloidal metal nanoparticles based assays

Biosensors and Bioelectronics 114 (2018) 124–45  
Contents lists available at ScienceDirect  
Biosensors and Bioelectronics  
journal homepage: www.elsevier.com/locate/bios

Plasmonic colorimetric sensors based on etching and growth of noble metal nanoparticles: Strategies and applications  
Zhiyang Zhang<sup>a,d</sup>, Han Wang<sup>a,c</sup>, Zhaopeng Chen<sup>a,c</sup>, Xiaoyan Wang<sup>a</sup>, Jiebum Choo<sup>a,c</sup>, Lingxin Chen<sup>a,c</sup>

Sensors and Actuators B: Chemical 292 (2019) 1261–1271  
Contents lists available at ScienceDirect  
Sensors and Actuators B: Chemical  
journal homepage: www.elsevier.com/locate/sab

Colorimetric detection of sugars based on gold nanoparticle formation  
Gerardo Palazzo<sup>a</sup>, Laura Facchini<sup>a</sup>, Antonia Mallardi<sup>a</sup>

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 217 (2019) 1207–1213  
Contents lists available at ScienceDirect  
Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy  
journal homepage: www.elsevier.com/locate/saa

Colorimetric detection of glucose based on gold nanoparticles coupled with silver nanoparticles  
Yan Gao, Yiting Wu, Junwei Di

Optical nanoprobe based on gold nanoparticles for sugar sensing  
Matteo Scamporrino, Alessandra Arcechi and Saverio Mannino

SCIENTIFIC REPORTS  
OPEN  
Multicolor Colorimetric Biosensor for the Determination of Glucose based on the Etching of Gold Nanorods  
Yue Liu<sup>a</sup>, Mengmeng Zhao<sup>a</sup>, Yiqian Guo<sup>a</sup>, Xiaoming Wu<sup>a</sup>, Fang Luo<sup>a</sup>, Lianhua Guo<sup>a</sup>, Wen Guo<sup>a</sup>, Guozhen Chen<sup>a</sup> & Zhenyu Liu<sup>a</sup>

Sensors and Actuators B: Chemical 292 (2019) 1261–1271  
Contents lists available at ScienceDirect  
Sensors and Actuators B: Chemical  
journal homepage: www.elsevier.com/locate/sab

A self-referenced optical colorimetric sensor based on silver and gold nanoparticles for quantitative determination of hydrogen peroxide  
Pedro J. Rivera<sup>a</sup>, Elia Ibañez<sup>a</sup>, Javier Goicoechea<sup>a</sup>, Aitor Utrilla<sup>a</sup>, Ignacio R. Marías<sup>a</sup>, Francisco J. Arregui<sup>a</sup>

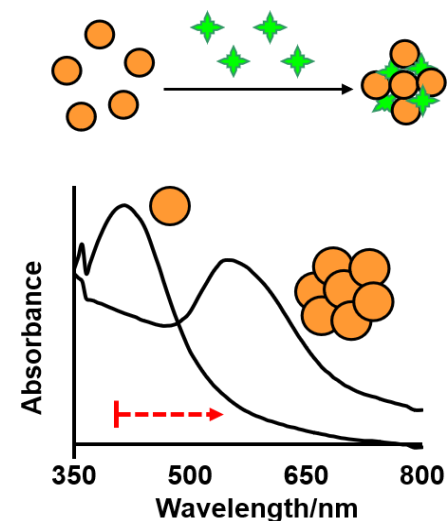
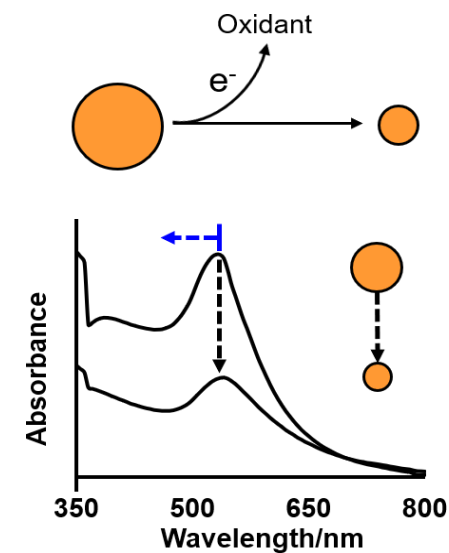
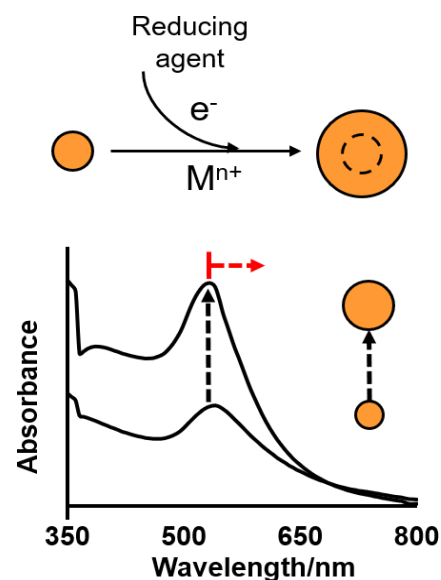
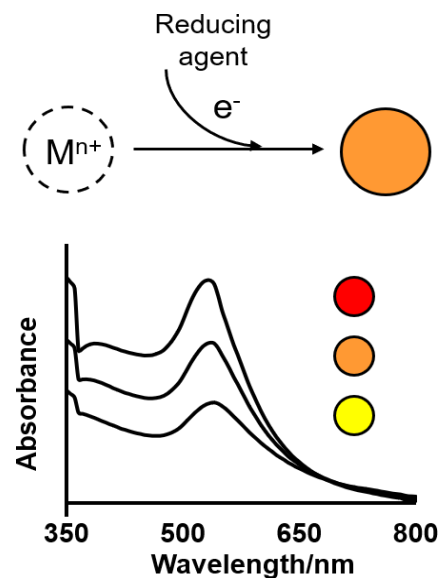
Analytica Chimica Acta 1000 (2018) 1–10  
Contents lists available at ScienceDirect  
Analytica Chimica Acta  
journal homepage: www.elsevier.com/locate/aca

Review  
Sensing colorimetric approaches based on gold and silver nanoparticles aggregation: Chemical creativity behind the assay. A review  
Diana Vilela, María Cristina González, Alberto Escarpa

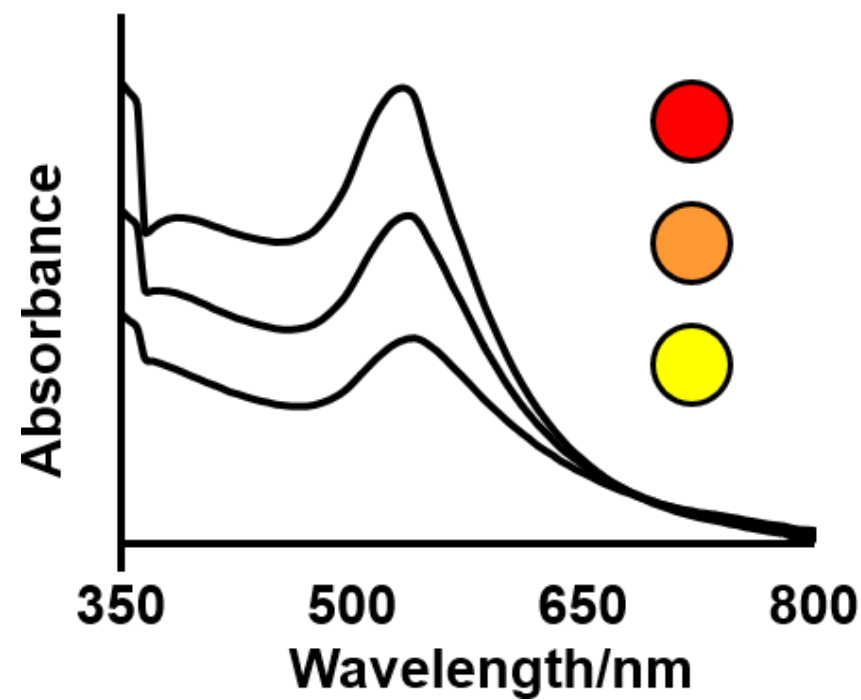
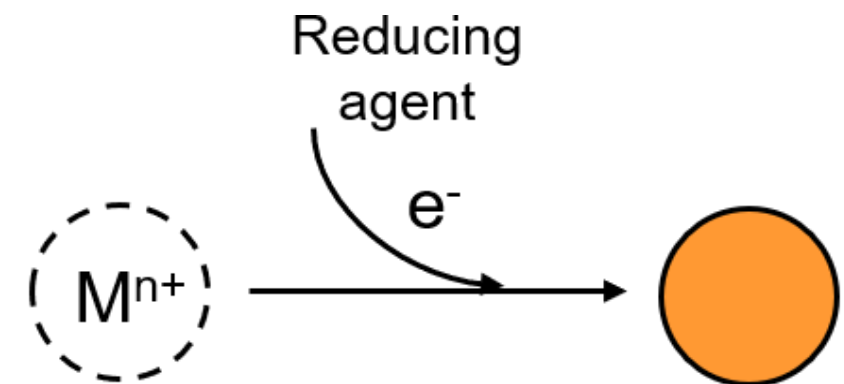
RSC Advances  
PAPER  
Sensitive colorimetric detection of glucose and cholesterol by using Au@Ag core-shell nanoparticles<sup>†</sup>  
Xuehong Zhang<sup>a</sup>, Min Wei<sup>a</sup>, Bingling Lu<sup>a</sup>, Yuanjin Liu<sup>a</sup>, Xu Liu<sup>a</sup> and Wei Wei<sup>a</sup>

Food Chemistry  
Volume 351, 30 July 2021, 129238  
Gold nanoparticle based colorimetric sensing strategy for the determination of reducing sugars  
Benedicta Brindusini<sup>a</sup>, Anton Popov<sup>a</sup>, Arcana Ramanaikumar<sup>a</sup>, Alina Ramanaikumar<sup>a</sup>

## Localized Surface Plasmon Resonance

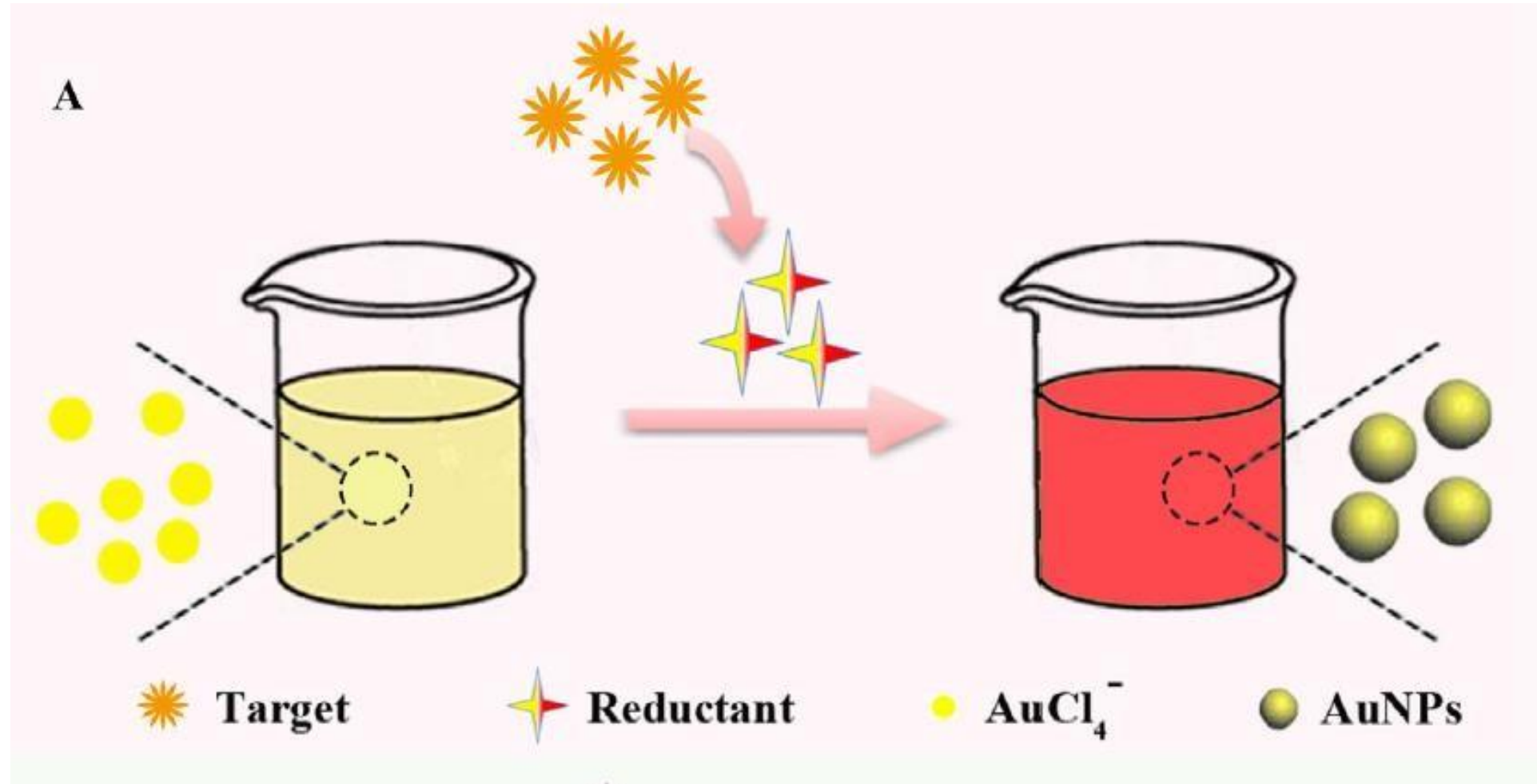


# Metal nanoparticles formation



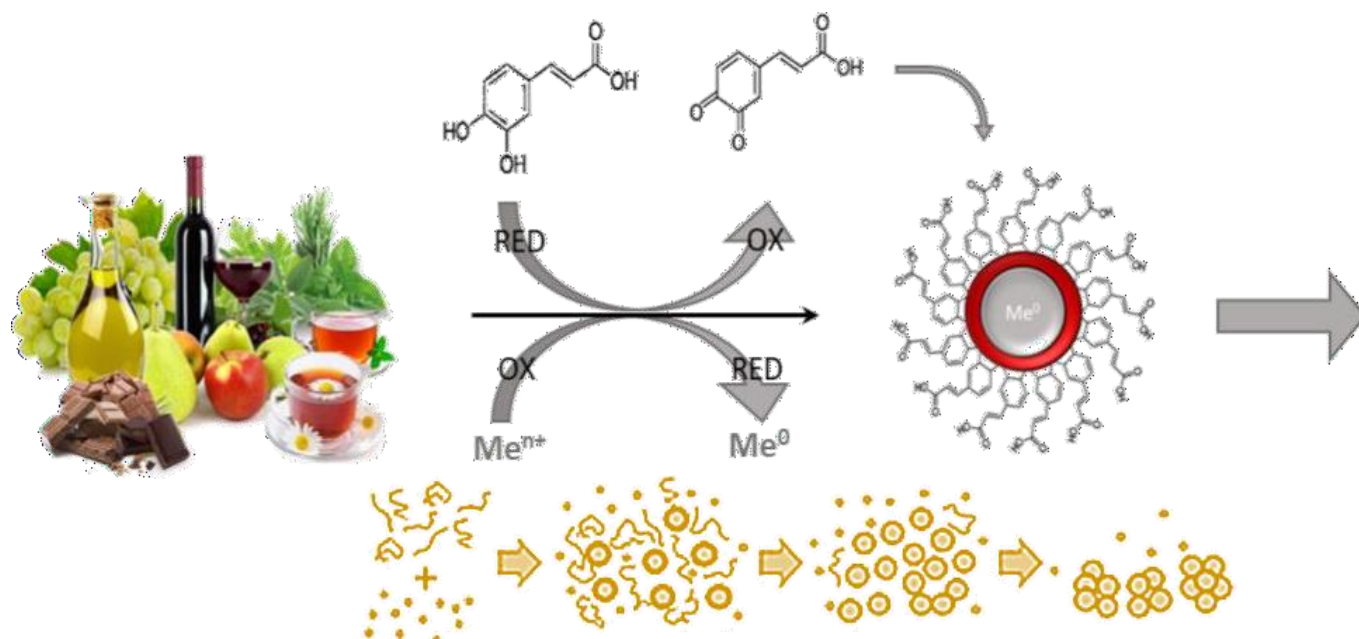
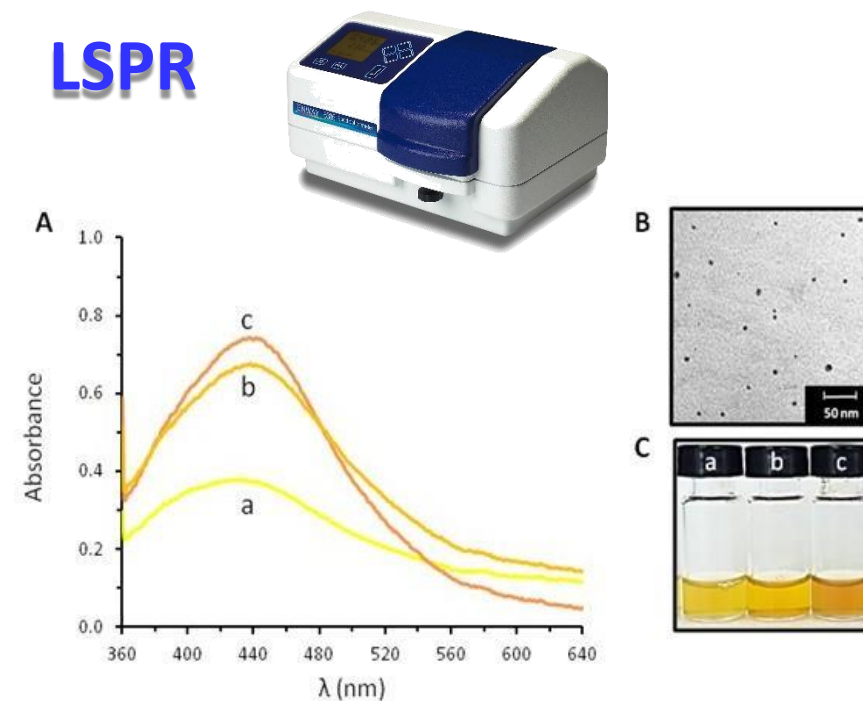
# Metal nanoparticles formation.

## Main strategy



# Metal nanoparticles formation

## Reducing compounds evaluation trough Au and AgNPs formation

**LSPR**

# Metal nanoparticles formation

## Phenolic content and antioxidant capacity evaluation through Au and AgNPs formation



Review

### Nanomaterial-Based Sensing and Biosensing of Phenolic Compounds and Related Antioxidant Capacity in Food

Flavio Della Pelle and Dario Compagnone \*

... Nanomaterial-based method for estimating the antioxidant activity relies on the polyphenol-mediated growth of MNPs (AuNPs and AgNPs), and optical monitoring of the corresponding plasmon absorption bands...

SCAMPICCHIO, Matteo, et al. Nanoparticle-based assays of antioxidant activity. *Analytical chemistry*, 2006, 78.6: 2060-2063.

Table 11.1: Food antioxidants.

Antioxidant	Subclasses	Formula	Examples	Sources
Phenolic acids	Hydroxybenzoic acids	$C_6-C_1$	Gallic acid, <i>p</i> -hydroxybenzoic acid, protocatechuic acid, vanillic acid, syringic acid	Blackberry, raspberry, tea
Flavonoids	Hydroxycinnamic acids	$C_6-C_3$	Caffeic acid, ferulic acid, <i>p</i> -coumaric acid, sinapic acid	Blueberry, coffee
	Flavonols	$C_6-C_3-C_6$	Quercetin, kaempferol	Onions, leeks, broccoli
	Flavones		Apigenin, luteolin	
Carotenoids	Flavanones	$C_{40}H_{56}O_n$	Naringenin, hesperetin, eriodictyol	Orange, grapefruit, lemon
	Flavanols		Catechin, epicatechin	Tea, chocolate
	Isoflavones		Genistein, daidzein, glycitein	Soy
	Anthocyanidins		Cyanidin, malvidin, delphinidin	Berries
Vitamins	Xanthophylls	$C_{40}H_{56}$	$\beta$ -Cryptoxanthin, lutein, zeaxanthin, neoxanthin, violaxanthin, $\alpha$ -cryptoxanthin	Peppers, green leafy vegetables
	Carotenes		$\alpha$ -Carotene, $\beta$ -carotene, lycopene	Pumpkin, carrot, tomato
	Vitamin C	$C_6H_8O_6$		Citrus fruits, kiwi, strawberry
	Vitamin E	$C_{29}H_{50}O_2$	Tocopherols, tocotrienols	Nuts, seeds, fish oil, whole grains



# Polyphenols sensing

AuNPs

AoC  
Hydrophilic  
Matrix Sample



- AoC evaluation
- The pH (8) avoid sugar interference
- High correlation with classical methods for antioxidant determination
- Sensitivity to intrinsic antioxidant power (o-diphenols most reactive)

Total assay time: 25 min

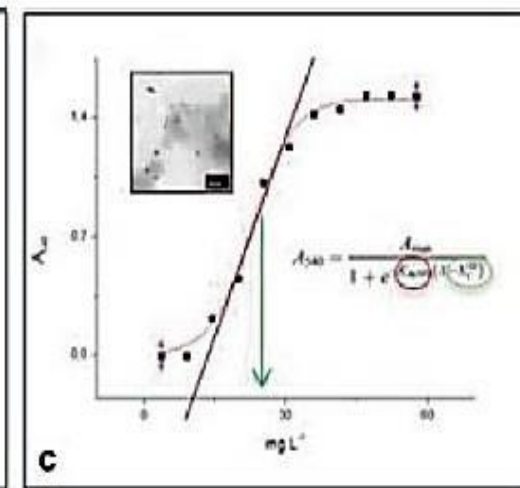
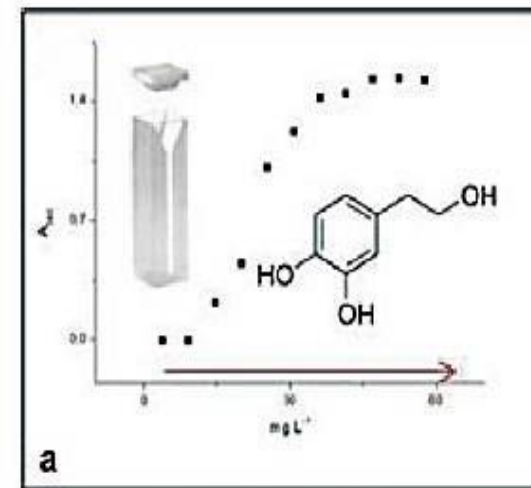
AuNPs

Fat

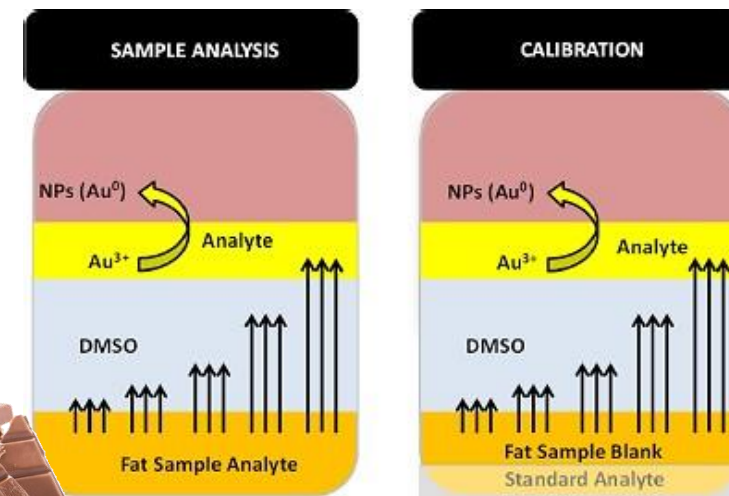
AoC  
Fat  
Matrix Sample

- Total polyphenols determination (40C°)
- Extraction free: directly applicable in fat sample matrix
- Low amount of sample is required (30 µL)
- Rapid and robust
- Sensitive

Total assay time: 10 min



DELLA PELLE, Flavio, et al. Development of an Optical Sensing Strategy Based on Gold Nanoparticles Formation Driven by Polyphenols. Application to Food Samples. In: *Sensors*. Springer, Cham, 2015. p. 39-46.

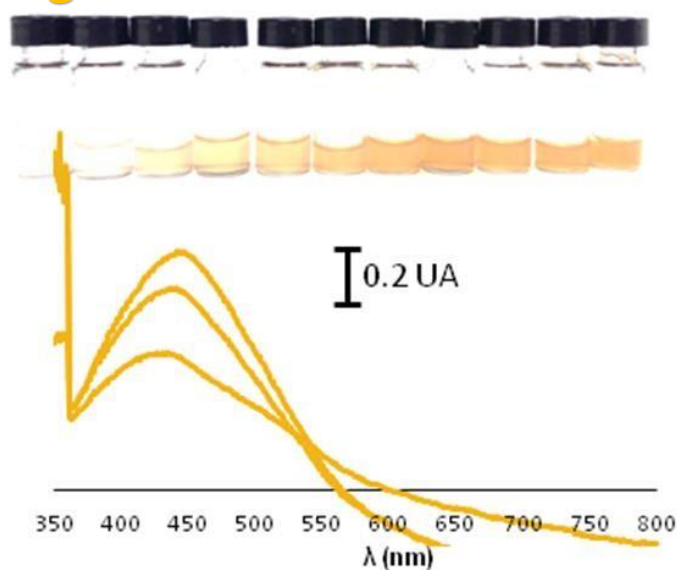


DELLA PELLE, Flavio, et al. Gold nanoparticles-based extraction-free colorimetric assay in organic media: an optical index for determination of total polyphenols in fat-rich samples. *Analytical chemistry*, 2015, 87.13: 6905-6911.

# Metal nanoparticles formation

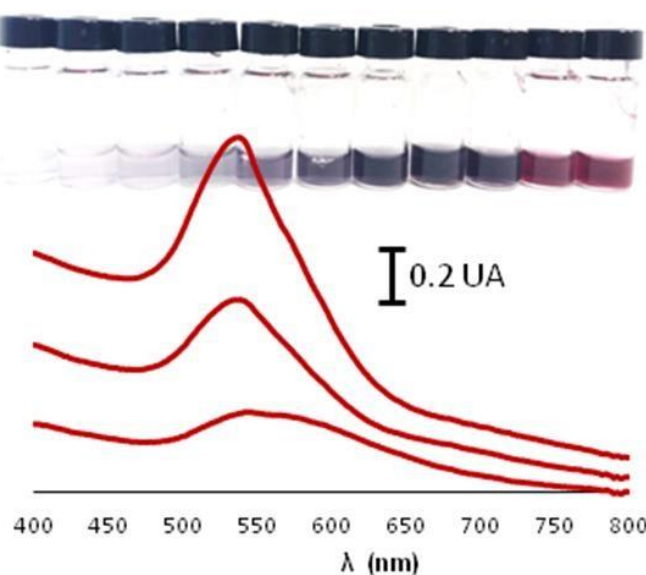
## Phenolic content and antioxidant capacity evaluation trough Au and AgNPs formation

### AgNPs

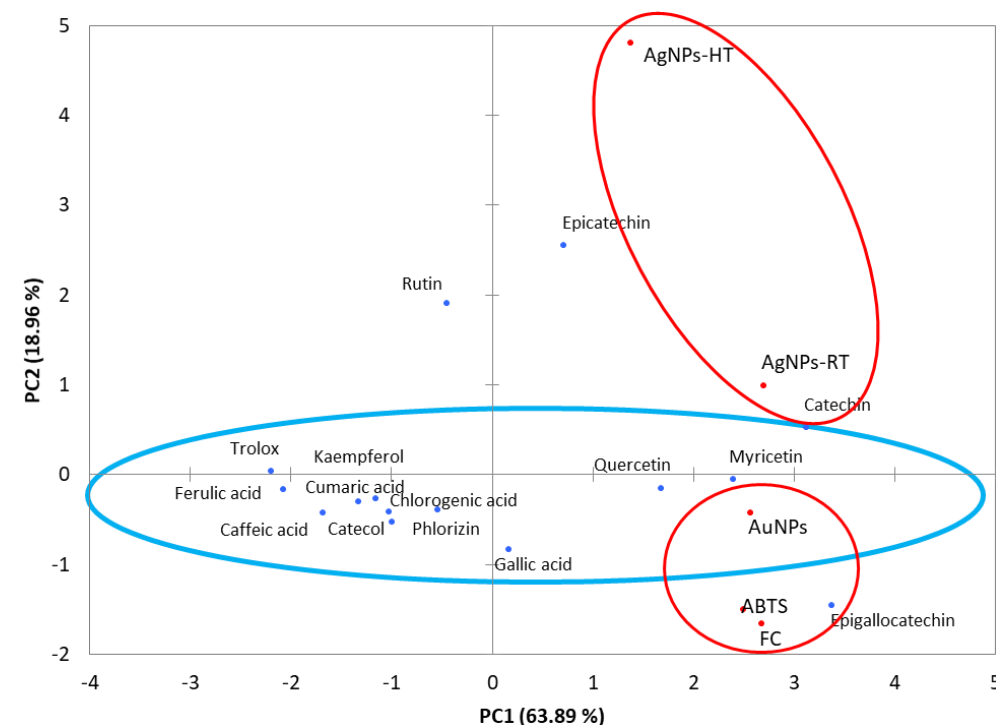


Epicatechin concentration:  
2, 4 and 6  $\mu$ M

### AuNPs



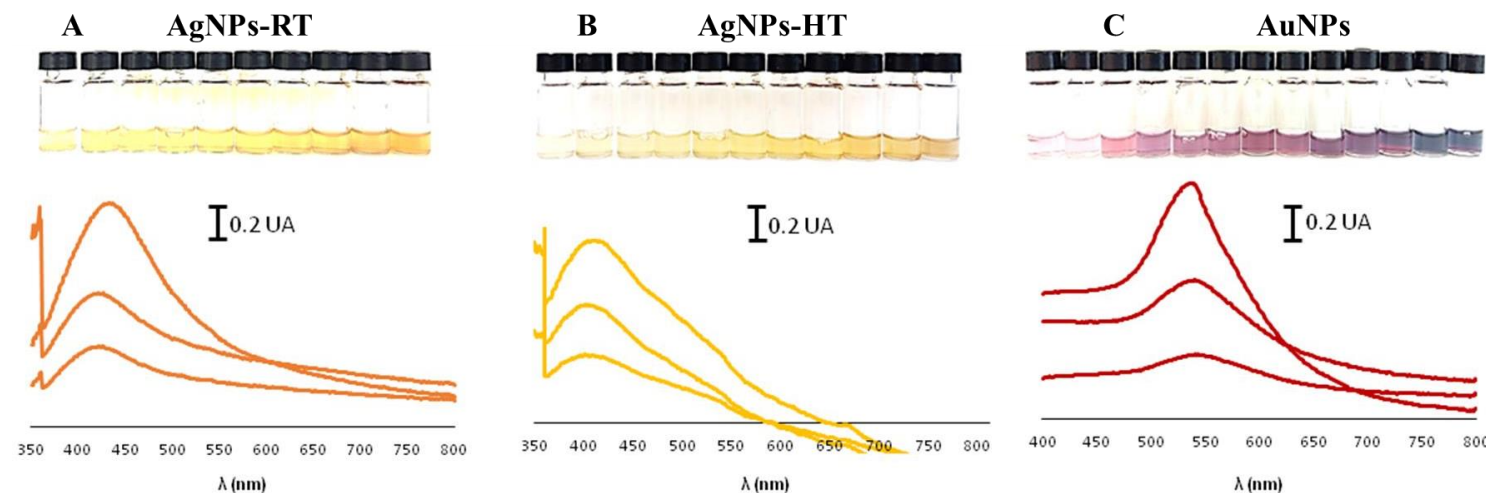
Epicatechin concentration:  
70, 90, 110  $\mu$ M



R	ABTS	FC	AgNPs-HT	AgNPs-RT	AuNPs
ABTS	1	0.876	0.891	0.956	0.977
FC	0.876	1	0.733	0.913	0.801
AgNPs-HT	0.891	0.733	1	0.770	0.826
AgNPs-RT	0.956	0.913	0.770	1	0.950
AuNPs	0.977	0.801	0.826	0.950	1

# Metal nanoparticles formation

## Phenolic content and antioxidant capacity evaluation in teas and infuses



MNPs spectra obtained with AgNPs-RT (A), AgNPs-HT (B) and AuNPs (C) assays using increasing volume of the sample 'RE' ('relax')



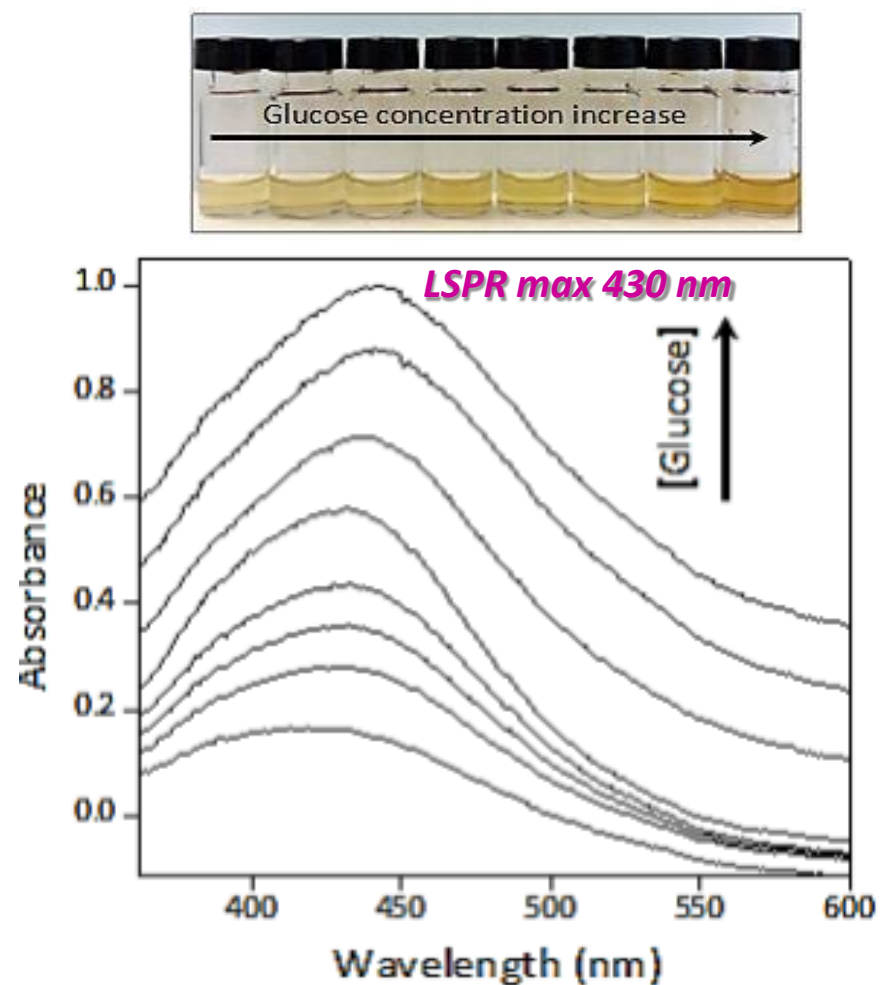
VT: Vanilla Tea  
TG: Green Tea  
TC: Classic Tea  
SD: sogni d'oro infused  
RE: Relax infused

RB: Rosa di bosco Infused  
LT: Lemon Tea  
IN: Finocchio infused  
DIG: Digestiva infused

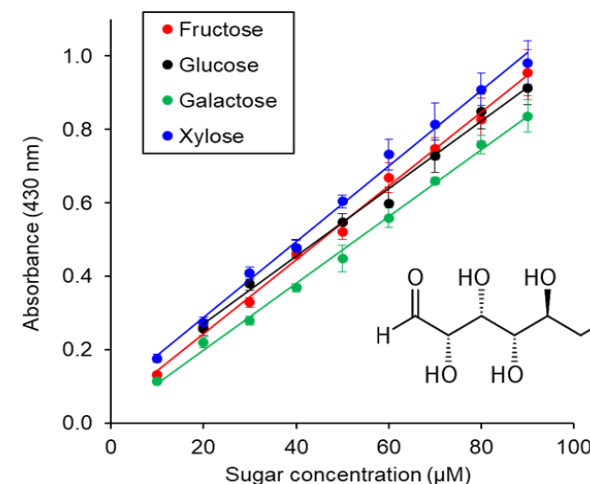
Sample Method	DIG (g Kg <sup>-1</sup> )	RSD (%)	IN (g Kg <sup>-1</sup> )	RSD (%)	LT (g Kg <sup>-1</sup> )	RSD (%)	RB (g Kg <sup>-1</sup> )	RSD (%)	RE (g Kg <sup>-1</sup> )	RSD (%)	SD (g Kg <sup>-1</sup> )	RSD (%)	TC (g Kg <sup>-1</sup> )	RSD (%)	TG (g Kg <sup>-1</sup> )	RSD (%)	VT (g Kg <sup>-1</sup> )	RSD (%)
AgNPs-RT	8.66	4	1.20	9	9.91	5	5.31	3	9.12	8	9.62	7	49.50	8	143.01	3	52.19	4
AgNPs-HT	11.10	9	12.52	9	14.73	5			7.78	10	6.98	14	13.33	6	24.42	7	7.82	12
AuNPs	18.63	5	1.52	7	15.64	2	15.86	5	15.58	7	14.03	5	20.56	6	132.35	3	27.95	4
ABTS	3.03	12	1.12	14	11.26	7	0.70	14	2.13	9	2.21	12	11.55	8	54.57	5	8.92	7
FC	5.98	4	2.51	11	14.54	3	3.70	10	5.51	4	5.42	5	21.10	7	30.54	8	16.79	6

# Metal nanoparticles formation

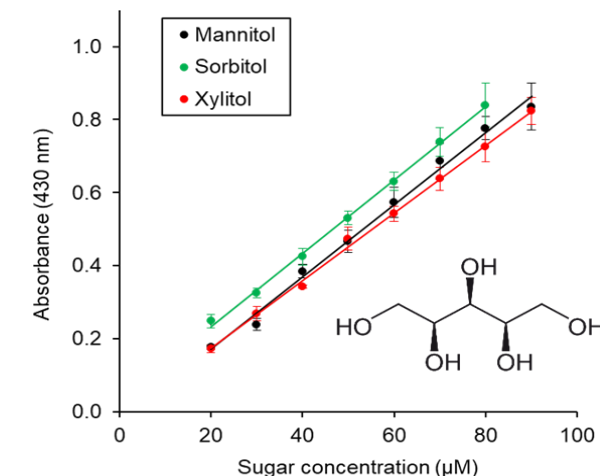
## Sugars content evaluation trough AgNPs formation



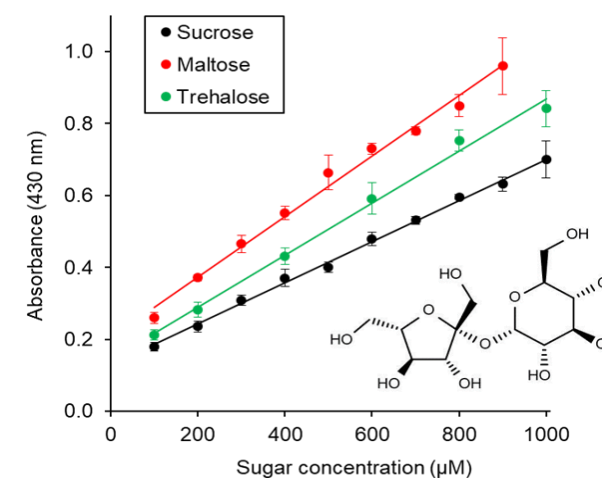
### Monosaccharides



### Polyols



### Diosaccharides

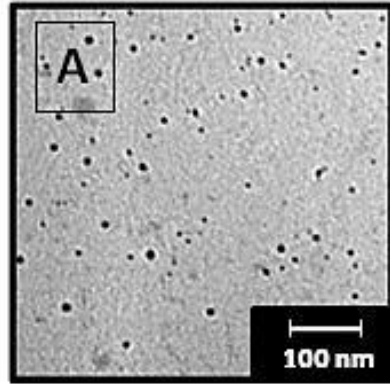




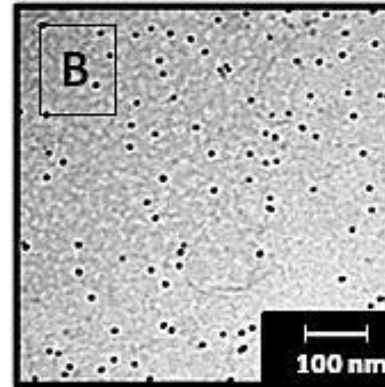
## AgNPs Morphological study

TEM

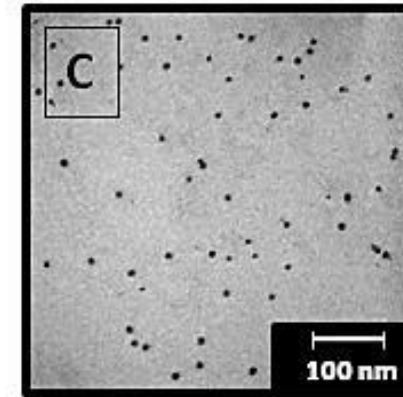
Glucose



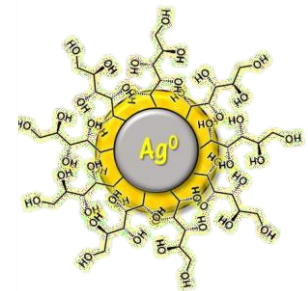
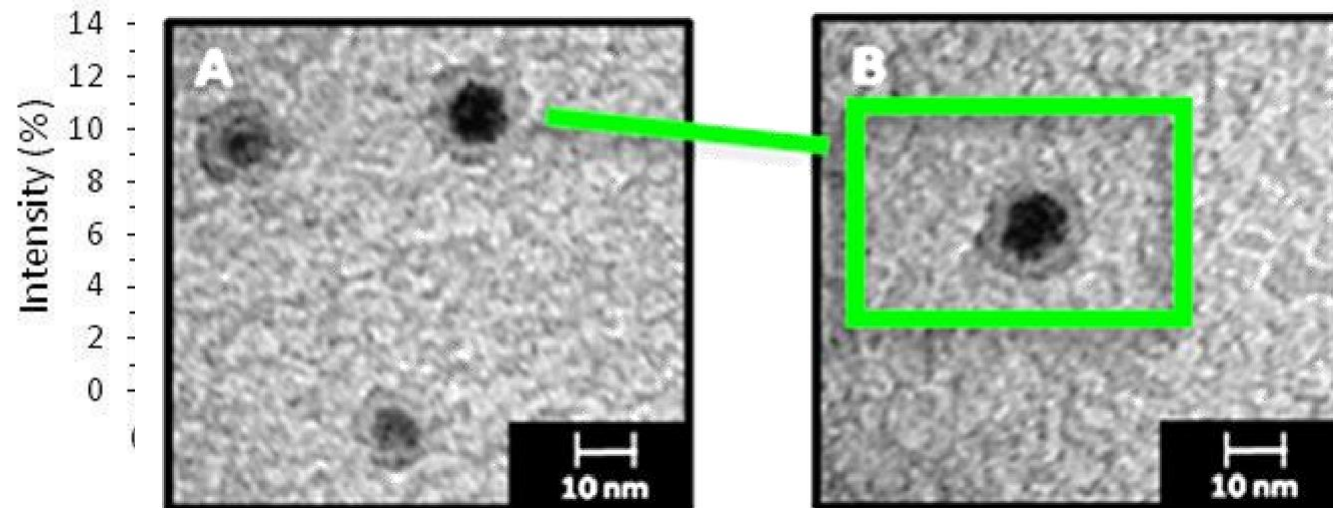
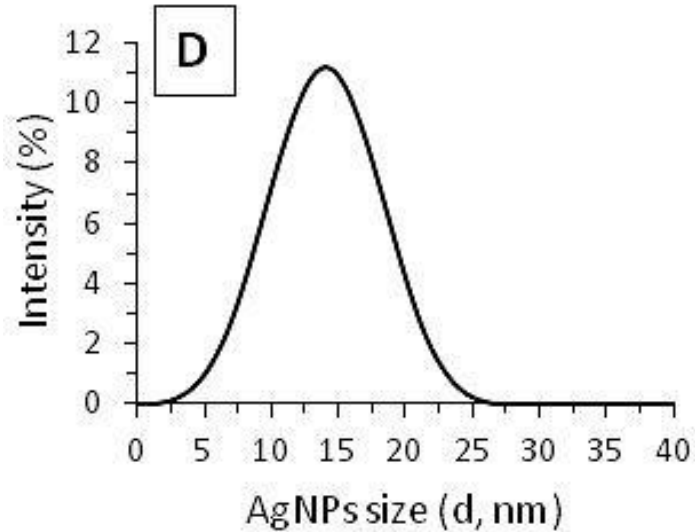
Sucrose



Xylitol



DLS



40



# Metal nanoparticles formation

## Determination of total sugars in real samples: AgNPs method vs. ion chromatography

### Sample analysis

#### Samples challenged

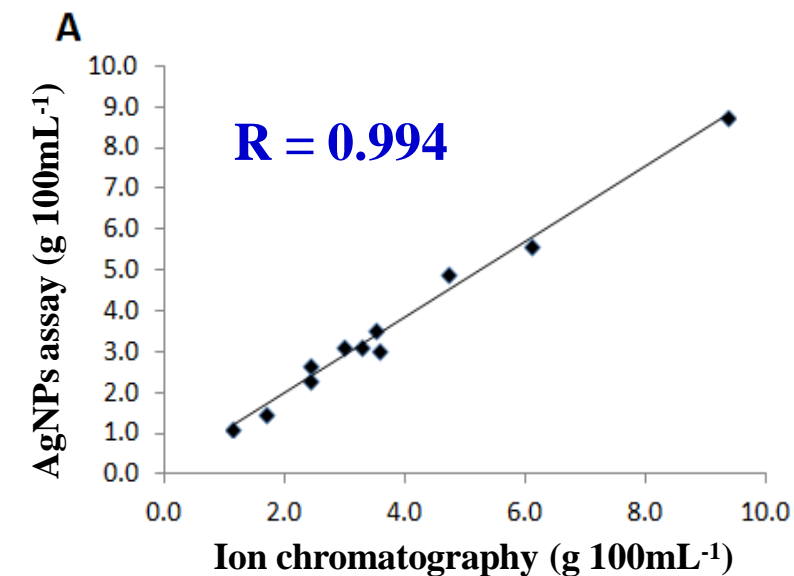
- Soft drinks n° 6
- Apple extracts n° 6



Sample	AgNPs assay (g 100 mL <sup>-1</sup> , Glu. Eq.)	RSD (%, n = 5)	Ion chromatography (g 100 mL <sup>-1</sup> , Glu + Fru)	RSD (%, n = 3)	AgNPs assay relative error (%)
Peach tea	2.98 ± 0.14	4.74	3.13 ± 0.08	2.71	+ 5.0
Black tea	3.56 ± 0.23	6.51	3.05 ± 0.11	3.56	- 14.3
Coconut water	4.72 ± 0.13	2.84	4.93 ± 0.05	0.98	+ 4.4
Gaseous	3.50 ± 0.25	7.23	3.53 ± 0.04	1.21	+ 0.9
Cedrata	9.36 ± 0.27	2.85	8.74 ± 0.78	8.9	- 6.6
Tonic water	6.11 ± 0.07	1.15	5.62 ± 0.12	2.11	- 8.0
Apple 1	1.67 ± 0.02	1.12	1.50 ± 0.02	1.11	- 10.2
Apple 2	1.14 ± 0.04	3.41	1.14 ± 0.02	1.78	0.0
Apple 3	3.27 ± 0.04	1.30	3.12 ± 0.10	3.10	- 4.6
Apple 4	2.43 ± 0.23	9.42	2.67 ± 0.11	4.10	+ 9.9
Apple 5	2.43 ± 0.02	0.74	2.31 ± 0.9	3.80	- 5.0

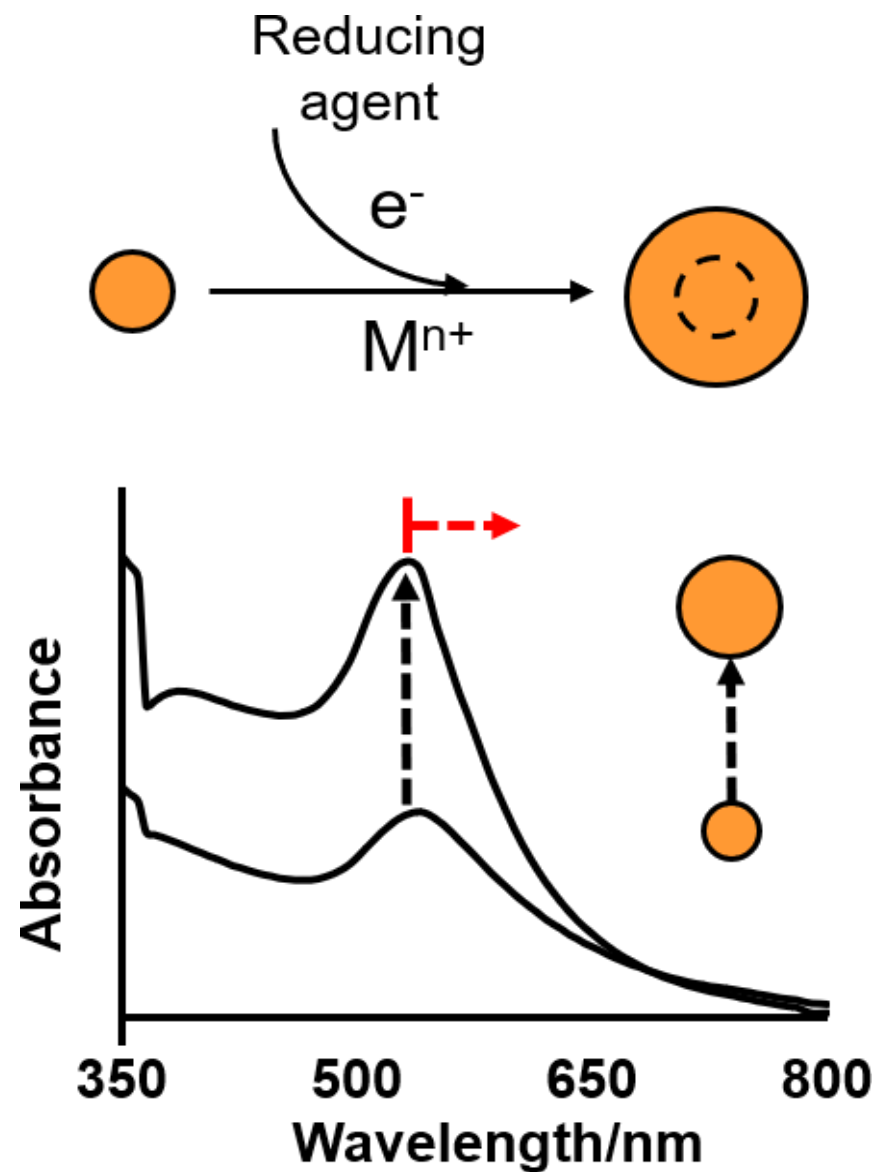
\* mean value n= 3

Rel. error between  
-14.9 and + 9.9 %

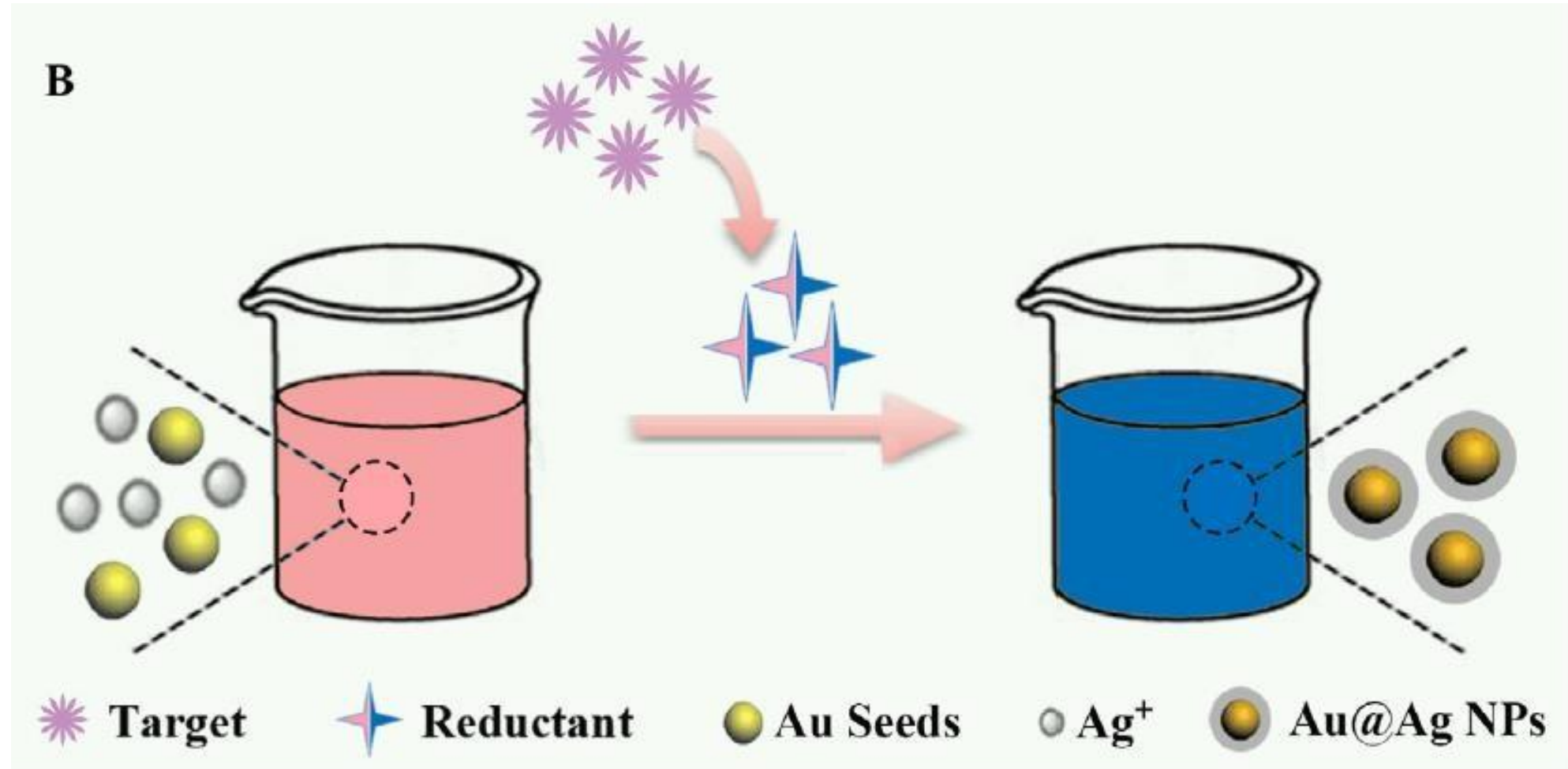


Recovery between 86 % and 118 %

## Metal nanoparticle- based seed-growth strategies

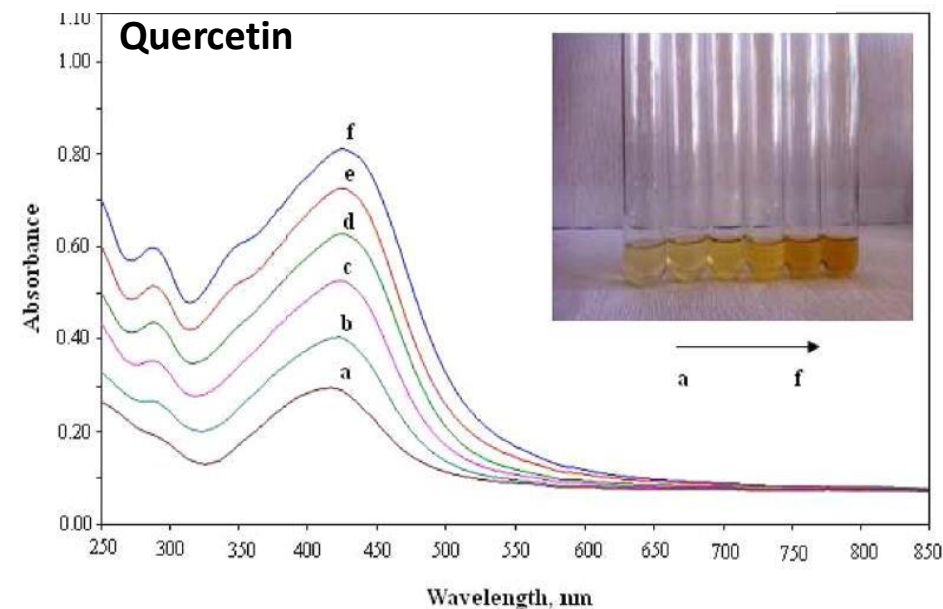
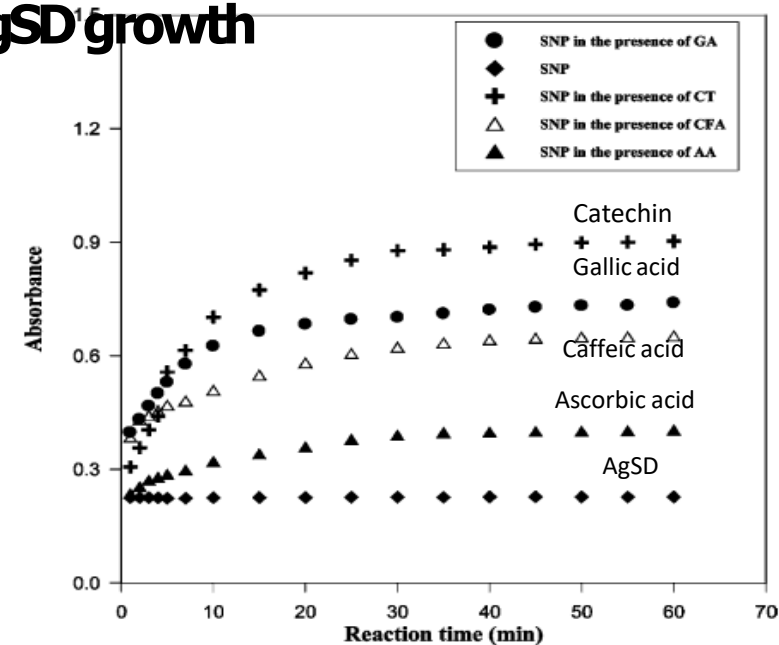
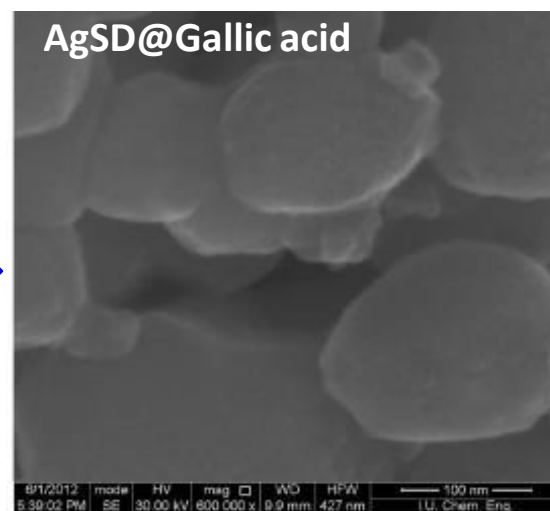
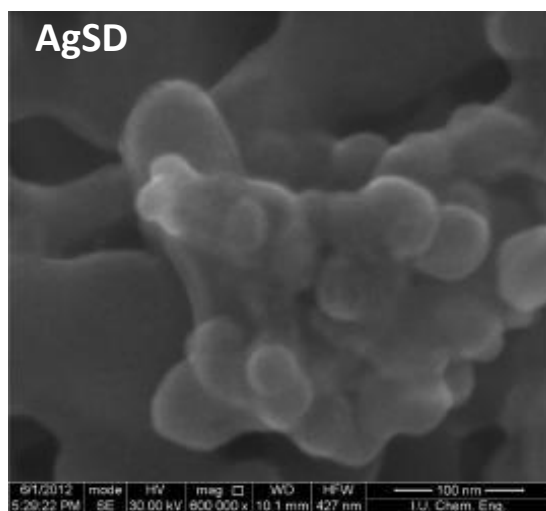
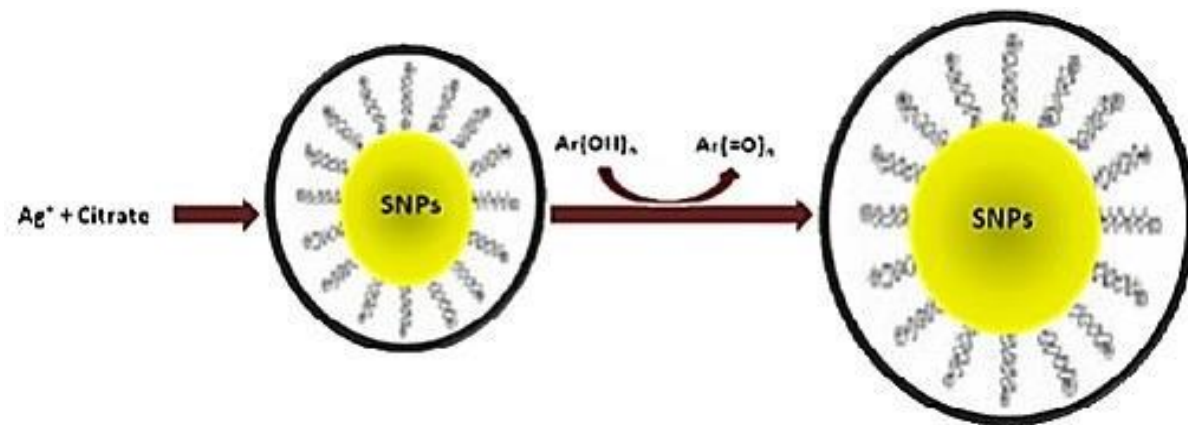


## Main strategy



# Metal nanoparticles growth

## Phenolic content and antioxidant capacity evaluation through AgSD<sup>16</sup> growth





# Metal nanoparticles growth

## Phenolic content and antioxidant capacity evaluation via AgSD growth

### Standards evaluation ad sample analysis

Table 1. Linear Equations, Correlation Coefficients (*r*), TEAC Coefficients,<sup>a</sup> and Linear Ranges for Antioxidants, with Respect to the Proposed SNPAC Method

antioxidants	linear equation and correlation coefficients	linear range (μM)	TEAC <sub>SNPAC</sub>	TEAC <sub>CUPRAC</sub> <sup>b</sup>
Simple Phenolic Acids				
gallic acid	$A = 2.27 \times 10^4c + 0.01$ ( $r = 0.9991$ )	1.67–52.30	2.91	2.62
Hydroxycinnamic Acids				
rosmarinic acid	$A = 3.90 \times 10^4c + 0.01$ ( $r = 0.9977$ )	1.02–30.51	5.02	5.30
caffeic acid	$A = 1.93 \times 10^4c + 0.02$ ( $r = 0.9990$ )	1.55–61.14	2.47	2.80
chlorogenic acid	$A = 2.37 \times 10^4c + 0.02$ ( $r = 0.9981$ )	1.26–49.79	3.04	2.47
Flavonols				
quercetin	$A = 2.99 \times 10^4c + 0.01$ ( $r = 0.9995$ )	1.33–39.80	3.83	4.38
fisetin	$A = 2.82 \times 10^4c - 0.019$ ( $r = 0.9978$ )	2.44–43.20	3.62	3.90
Flavan-3-ols				
ECG	$A = 4.16 \times 10^4c + 0.02$ ( $r = 0.9993$ )	0.72–28.36	5.33	5.30
EGCG	$A = 3.31 \times 10^4c + 0.02$ ( $r = 0.9994$ )	0.91–35.65	4.24	4.88
EC	$A = 2.70 \times 10^4c + 0.03$ ( $r = 0.9988$ )	0.74–43.33	3.46	2.77
catechin	$A = 2.82 \times 10^4c + 0.04$ ( $r = 0.9941$ )	0.35–41.13	3.61	3.09
EGC	$A = 2.84 \times 10^4c - 0.01$ ( $r = 0.9994$ )	2.11–42.60	3.64	3.34
Flavones				
luteolin	$A = 2.08 \times 10^4c + 0.03$ ( $r = 0.9952$ )	0.96–56.25	2.66	2.38
rutin	$A = 2.84 \times 10^4c + 0.03$ ( $r = 0.9974$ )	0.70–41.20	3.64	2.56
apigenin	$A = 1.92 \times 10^4c + 0.01$ ( $r = 0.9973$ )	2.19–62.10	2.47	0.12
Others				
ascorbic acid	$A = 1.13 \times 10^4c + 0.04$ ( $r = 0.9995$ )	0.88–103.00	1.44	0.96
α-tocopherol	$A = 1.04 \times 10^4c + 0.04$ ( $r = 0.9963$ )	0.96–111.00	1.33	1.10

<sup>a</sup>TEAC coefficients (significantly different) (by exclusion of the values for apigenin with highest TEAC variability;  $P = 0.05$ ,  $F_{exp} = 1.487$ ,  $F_{crit (table)} = 4.600$ ,  $F_{exp} < F_{crit (table)}$ ). <sup>b</sup>Data taken from refs 2 and 20.  $TEAC_{CUPRAC} = 1.16 TEAC_{SNPAC} - 0.782$  ( $r = 0.936$ ).

### Recovery study

Table 2. Precision and Recovery of the Proposed SNPAC Method

added conc (μM)	mean (μM)	stand dev, SD	rel stand dev, RSD (%)	REC (%) <sup>a</sup>
RT Addition to Green Tea				
5.43	$5.15 \pm 0.09$	0.04	0.78	94.8
10.86	$10.42 \pm 0.17$	0.07	0.67	96.0
21.72	$21.16 \pm 0.20$	0.08	0.38	97.4
CT Addition to Green Tea				
3.66	$3.48 \pm 0.22$	0.09	2.61	95.1
7.32	$7.52 \pm 0.19$	0.08	1.06	102.7
14.64	$14.82 \pm 0.20$	0.08	0.54	101.2
GA Addition to Green Tea				
4.65	$4.67 \pm 0.22$	0.09	1.93	100.2
9.30	$9.14 \pm 0.10$	0.04	0.44	98.3
18.6	$18.18 \pm 0.17$	0.07	0.36	97.7
CT Addition to Olive Oil				
3.66	$3.38 \pm 0.16$	0.06	1.87	92.3
7.32	$6.91 \pm 0.12$	0.05	0.72	94.4
14.64	$14.07 \pm 0.10$	0.04	0.28	96.1

<sup>a</sup>Recovery ( $N = 3$ ).

### Methods reliability

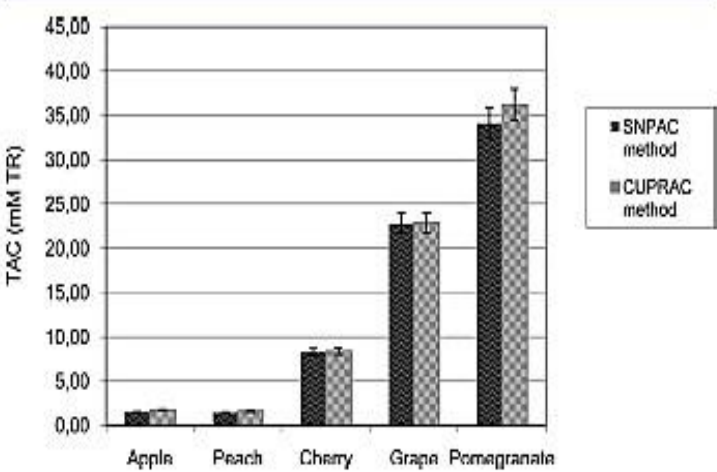


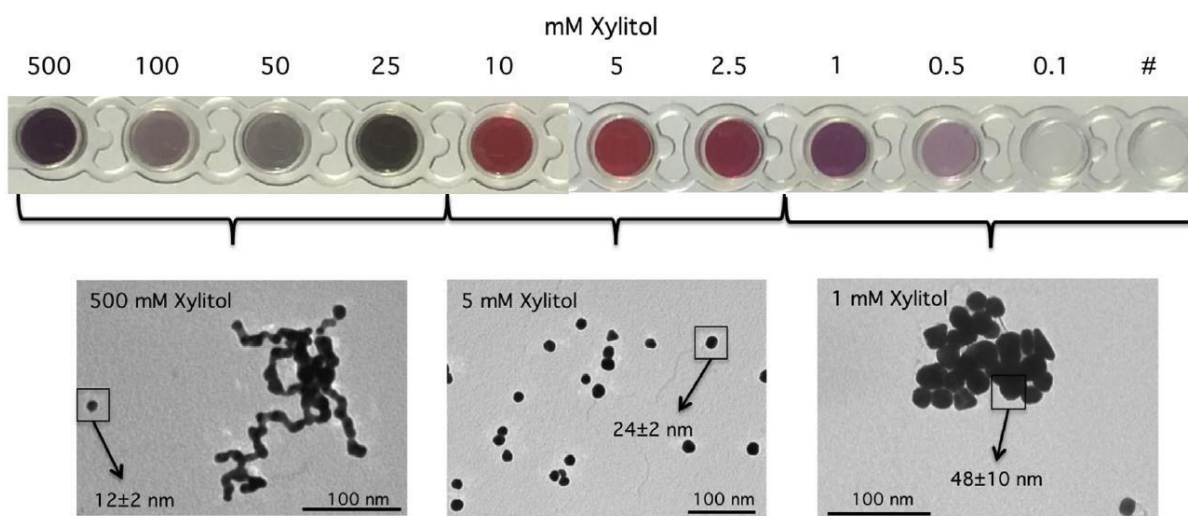
Figure 5. Comparative TAC values (mM TR equiv) of some commercial fruit juices measured by the SNPAC and CUPRAC assays. Data are presented as (mean  $\pm$  SD) (error bars),  $N = 3$ . ( $P = 0.05$ ,  $F_{exp} = 0.775$ ,  $F_{crit (table)} = 7.709$ ,  $F_{exp} < F_{crit (table)}$ .)



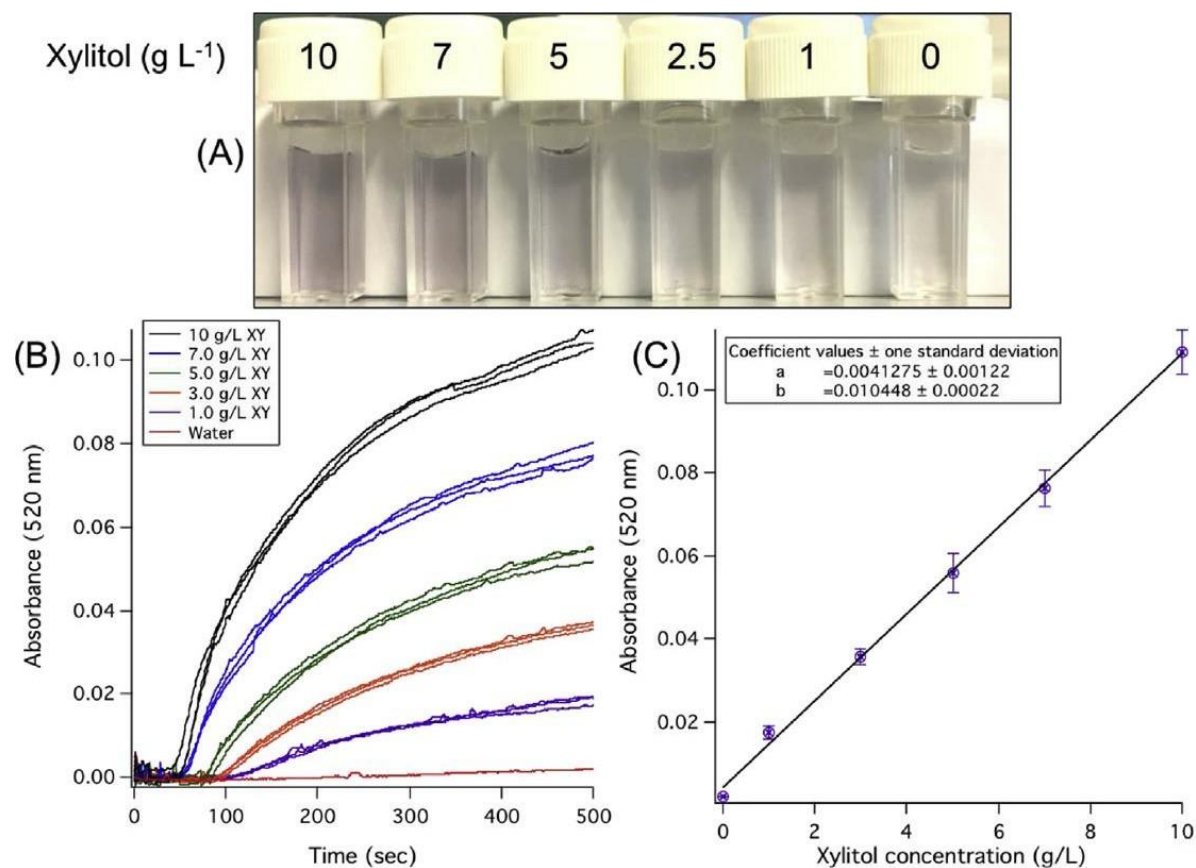
# Metal nanoparticles growth

## Xylitol monitoring through AuNPs growth

### Seed formation and growth phenomena study



### Dose-response kinetic and curve



Analytica Chimica Acta xxx (2017) 1–8

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Analytica Chimica Acta

journal homepage: [www.elsevier.com/locate/aca](http://www.elsevier.com/locate/aca)



The early nucleation stage of gold nanoparticles formation in solution as powerful tool for the colorimetric determination of reducing agents: The case of xylitol and total polyols in oral fluid

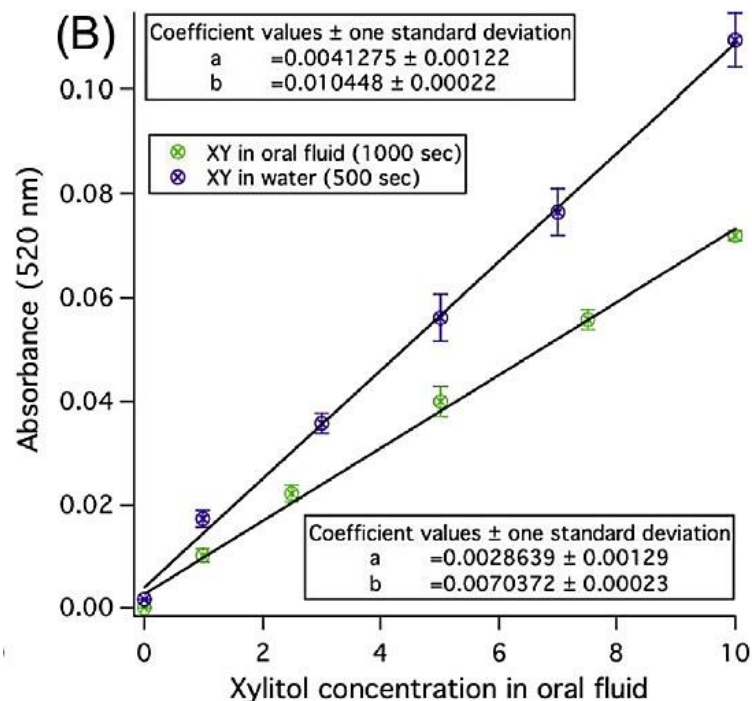
S. Scarano\*, E. Pascale, M. Minunni

# Metal nanoparticles growth

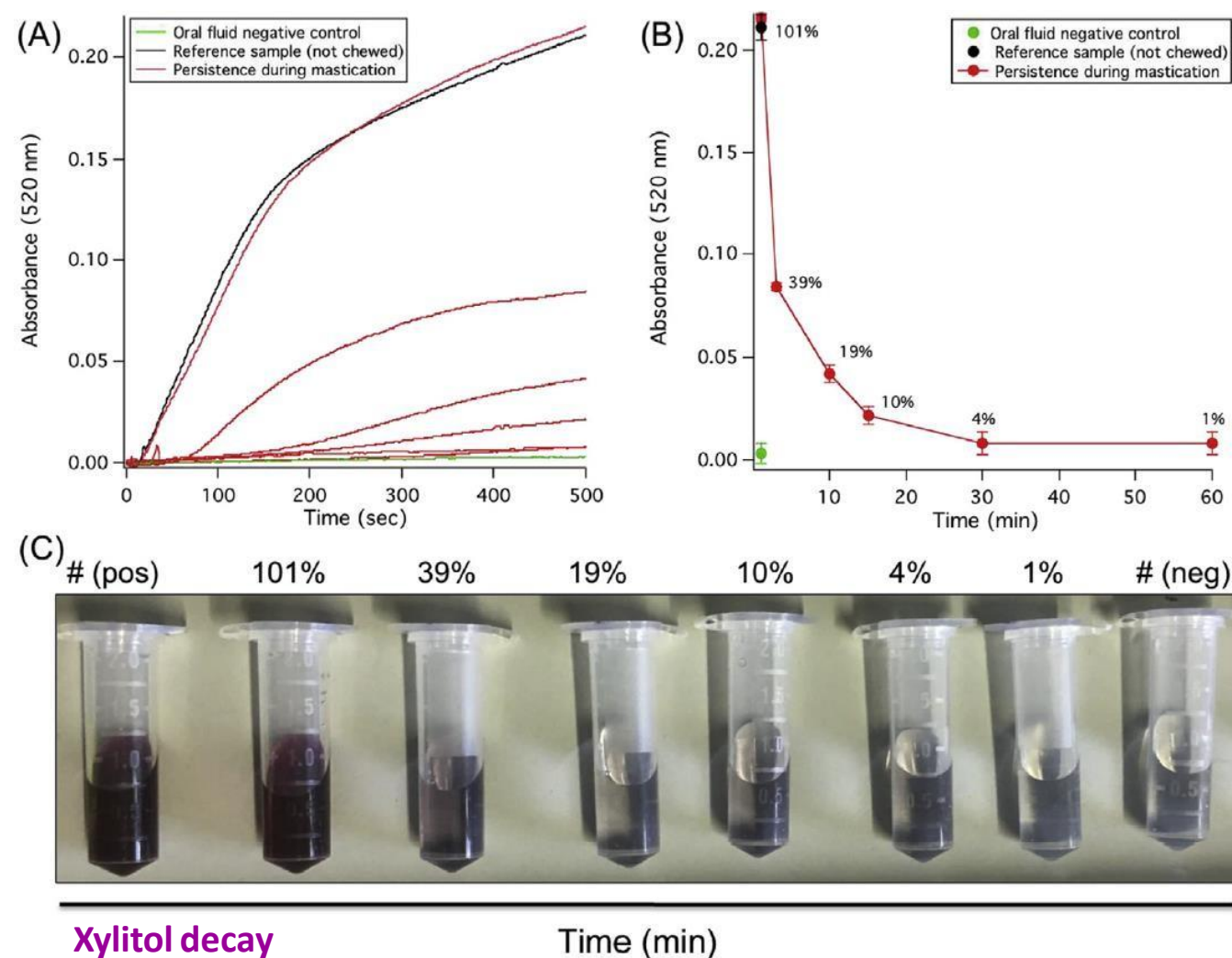
## Xylitol monitoring in human saliva through AuNPs growth

### Recovery study

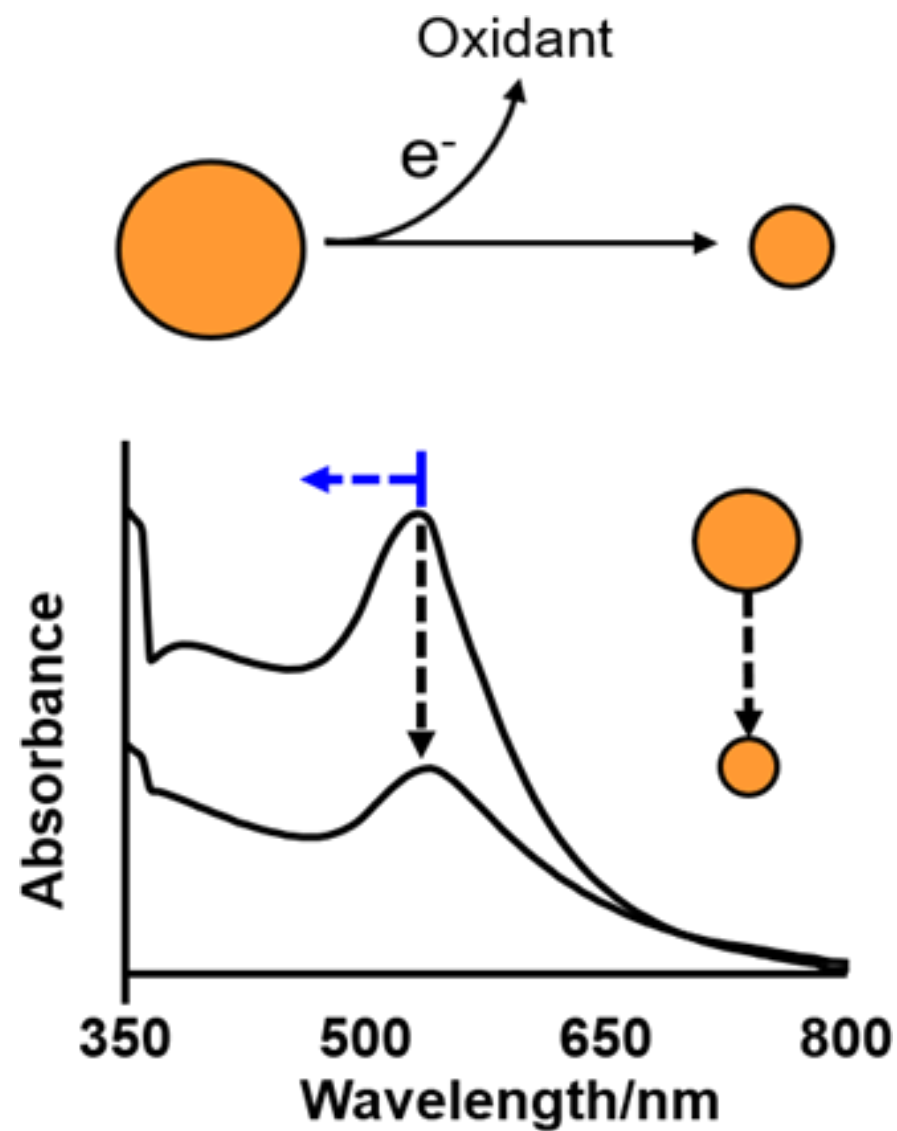
Methods evaluation for sample analysis



### Xylitol monitoring 1 h of chewing-gum

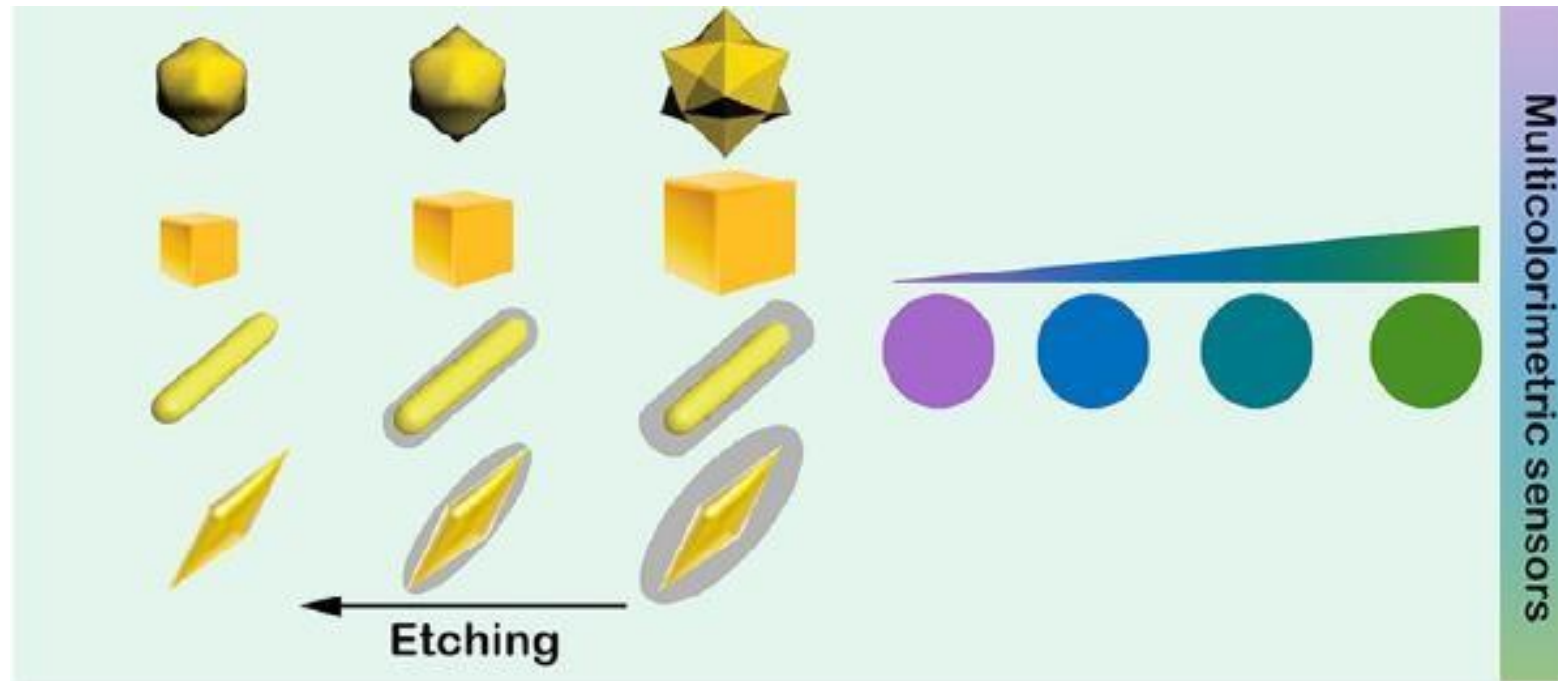
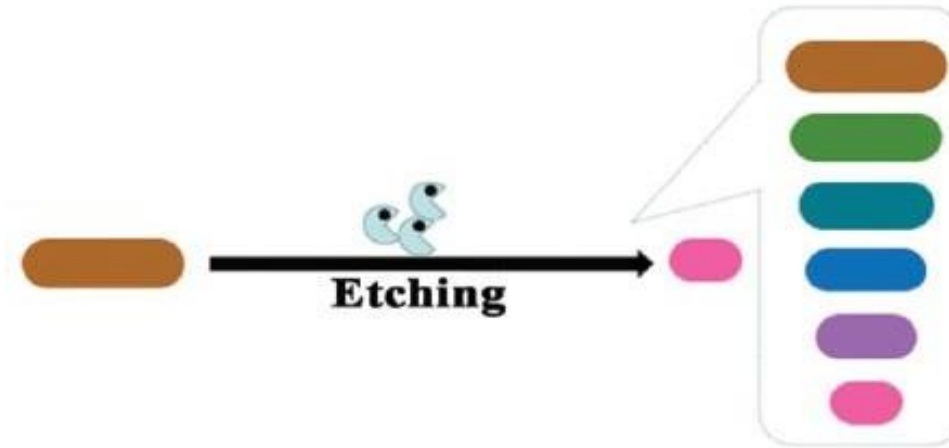


## Metal nanoparticle etching



# Metal nanoparticles etching

## Main strategy

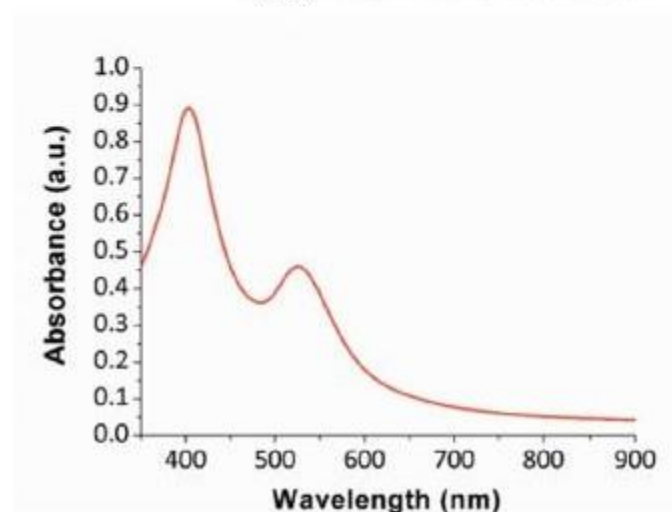
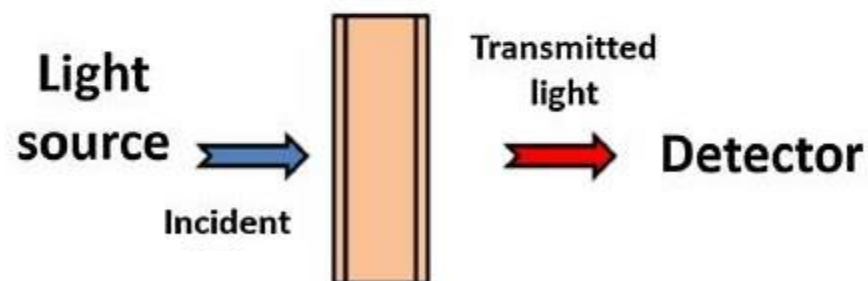
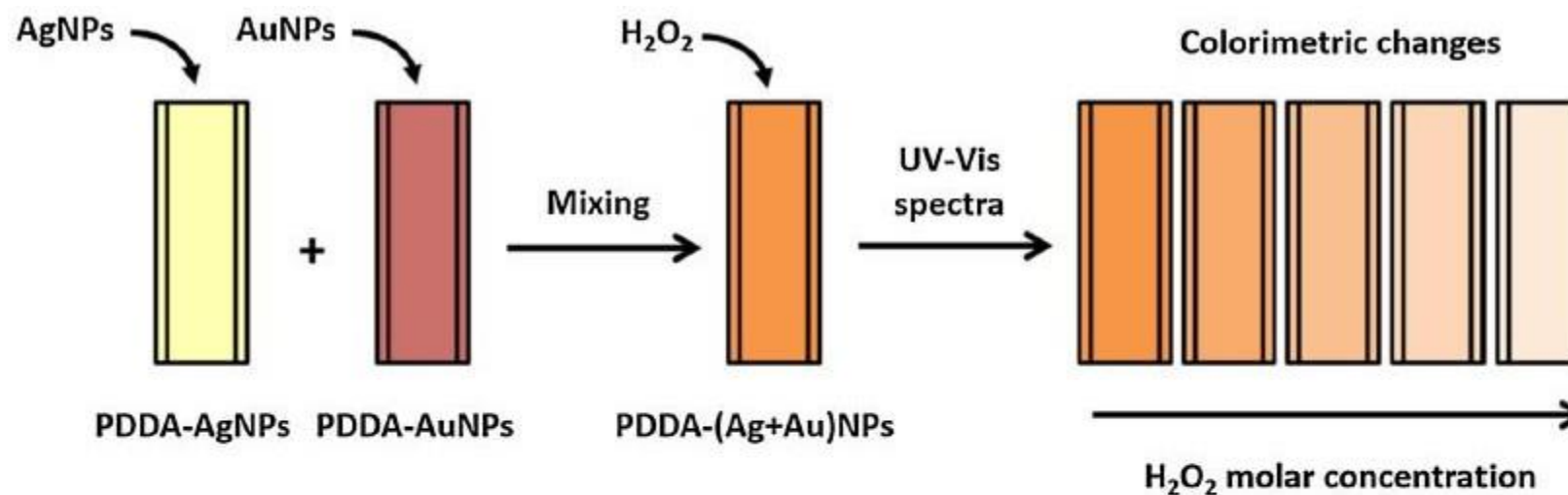




# Metal nanoparticles etching

## H<sub>2</sub>O<sub>2</sub> determination through MNPs etching

PDDA- Poly(diallyldimethylammoniumchloride)



Sensors and Actuators B 251 (2017) 624–631

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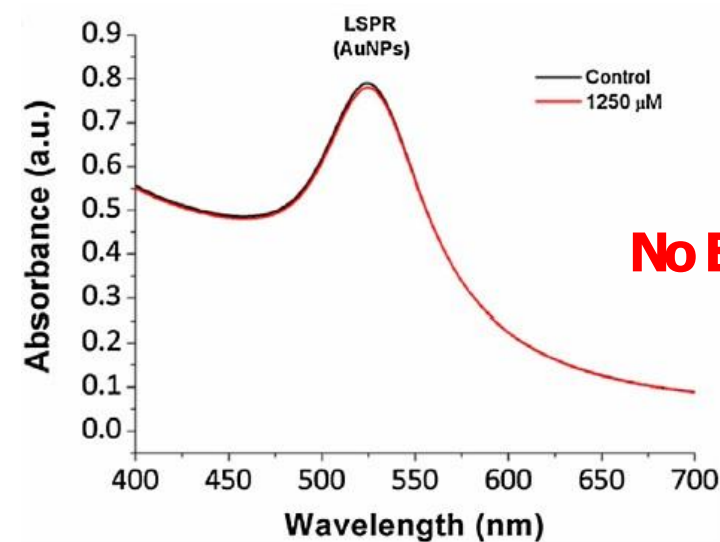
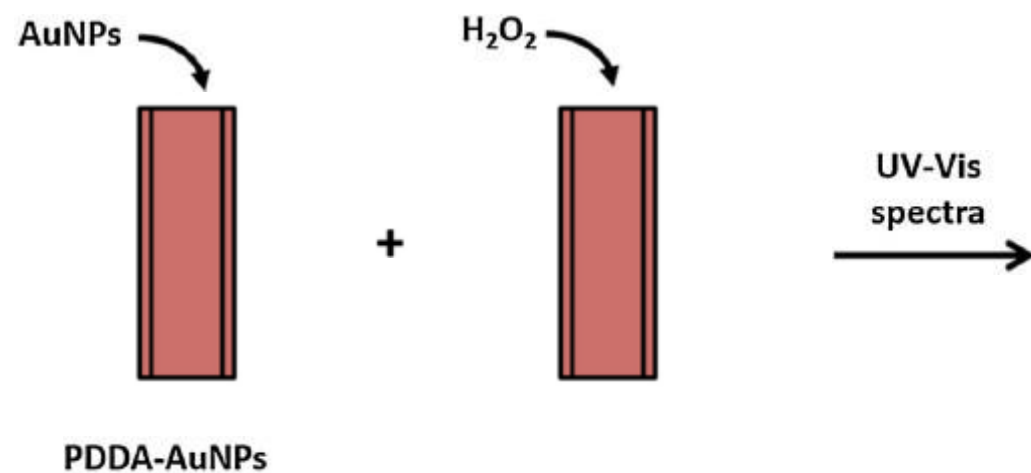
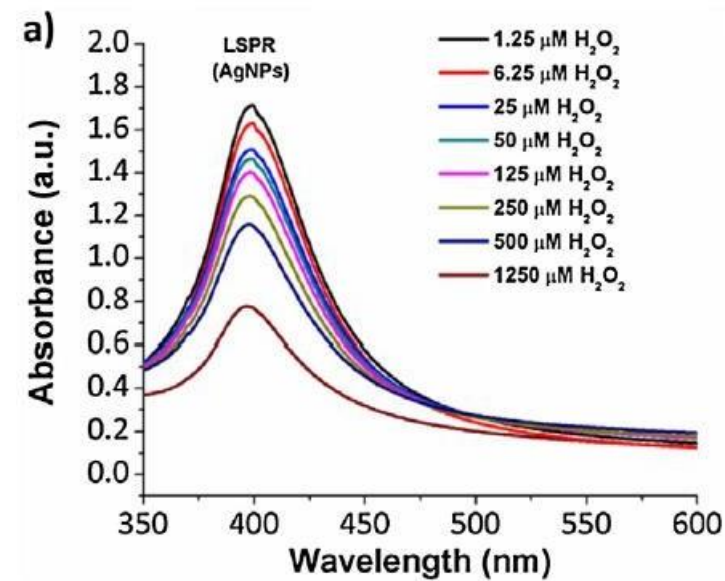
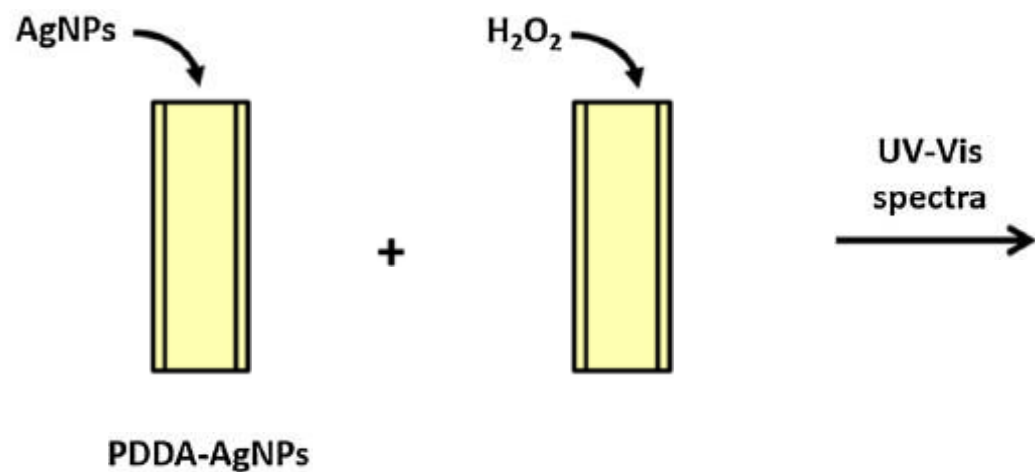
A self-referenced optical colorimetric sensor based on silver and gold nanoparticles for quantitative determination of hydrogen peroxide

Pedro J. Rivero<sup>a,\*</sup>, Elia Ibañez<sup>b</sup>, Javier Goicoechea<sup>b</sup>, Aitor Urrutia<sup>b</sup>, Ignacio R. Matias<sup>c</sup>, Francisco J. Arregui<sup>b</sup>



# Metal nanoparticles etching

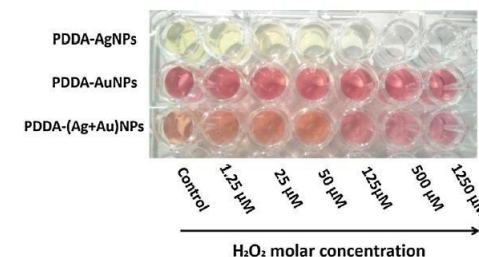
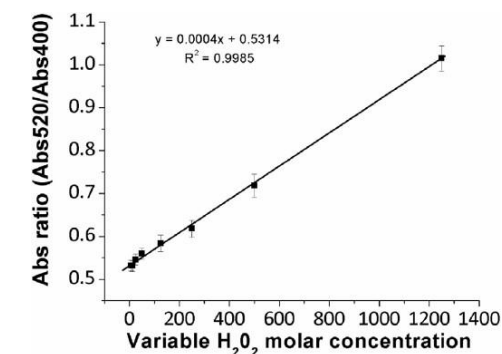
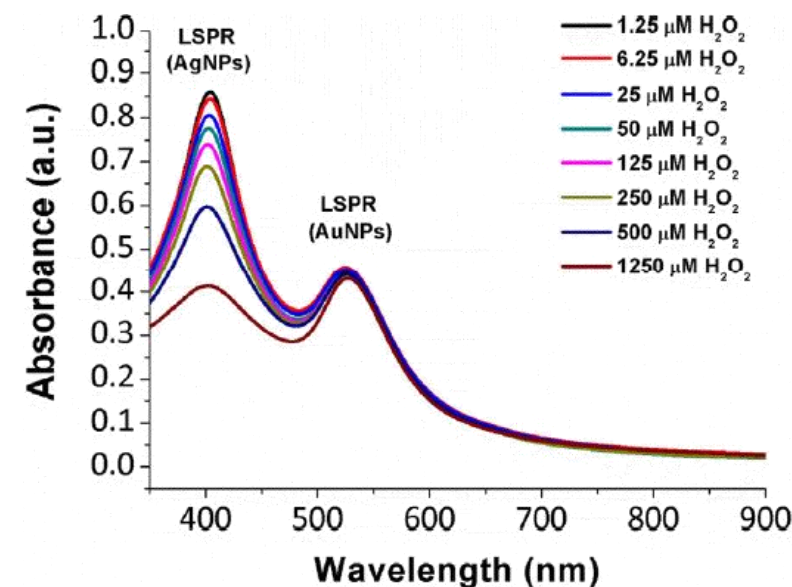
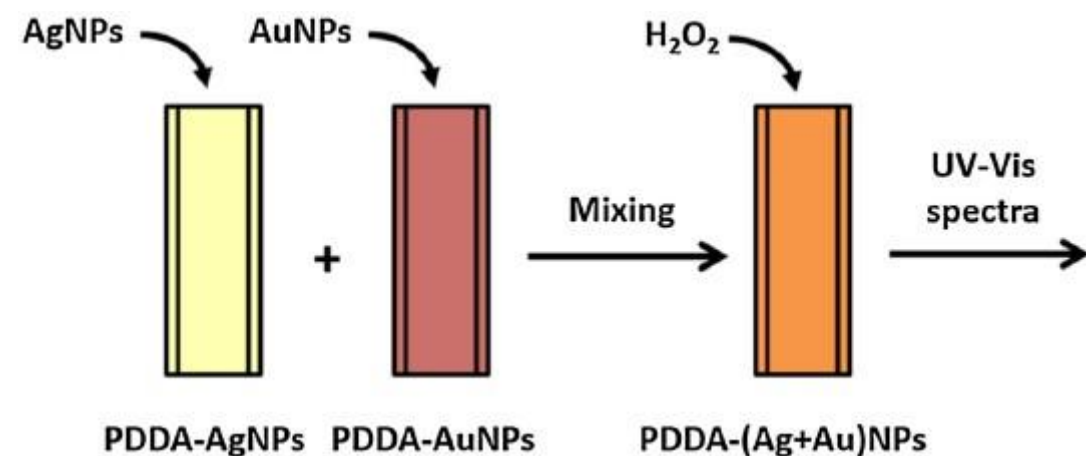
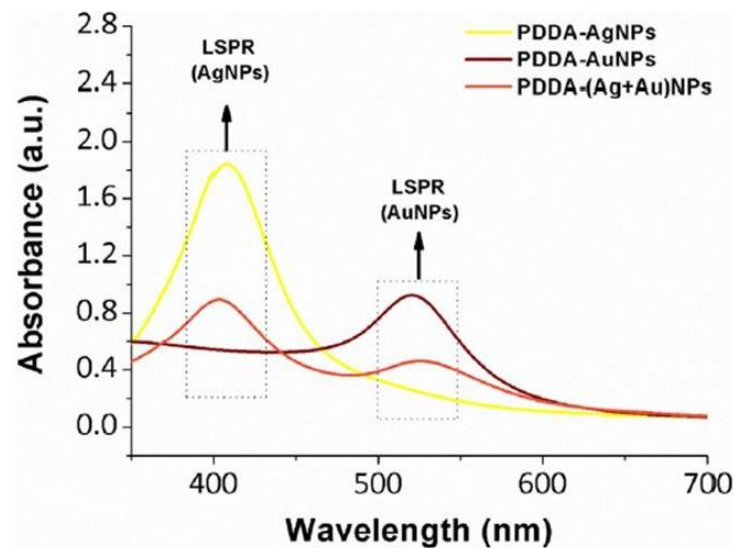
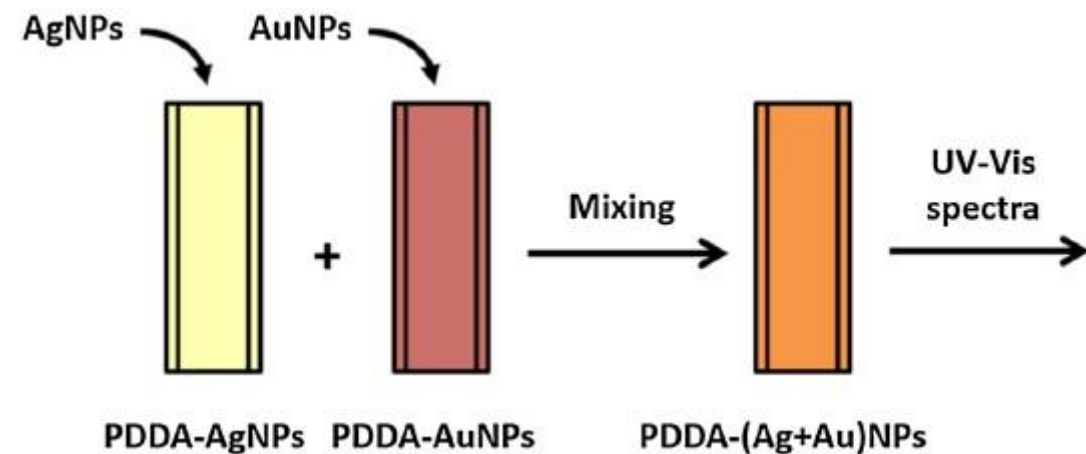
## Etching phenomena study



**No Etching phenomena**

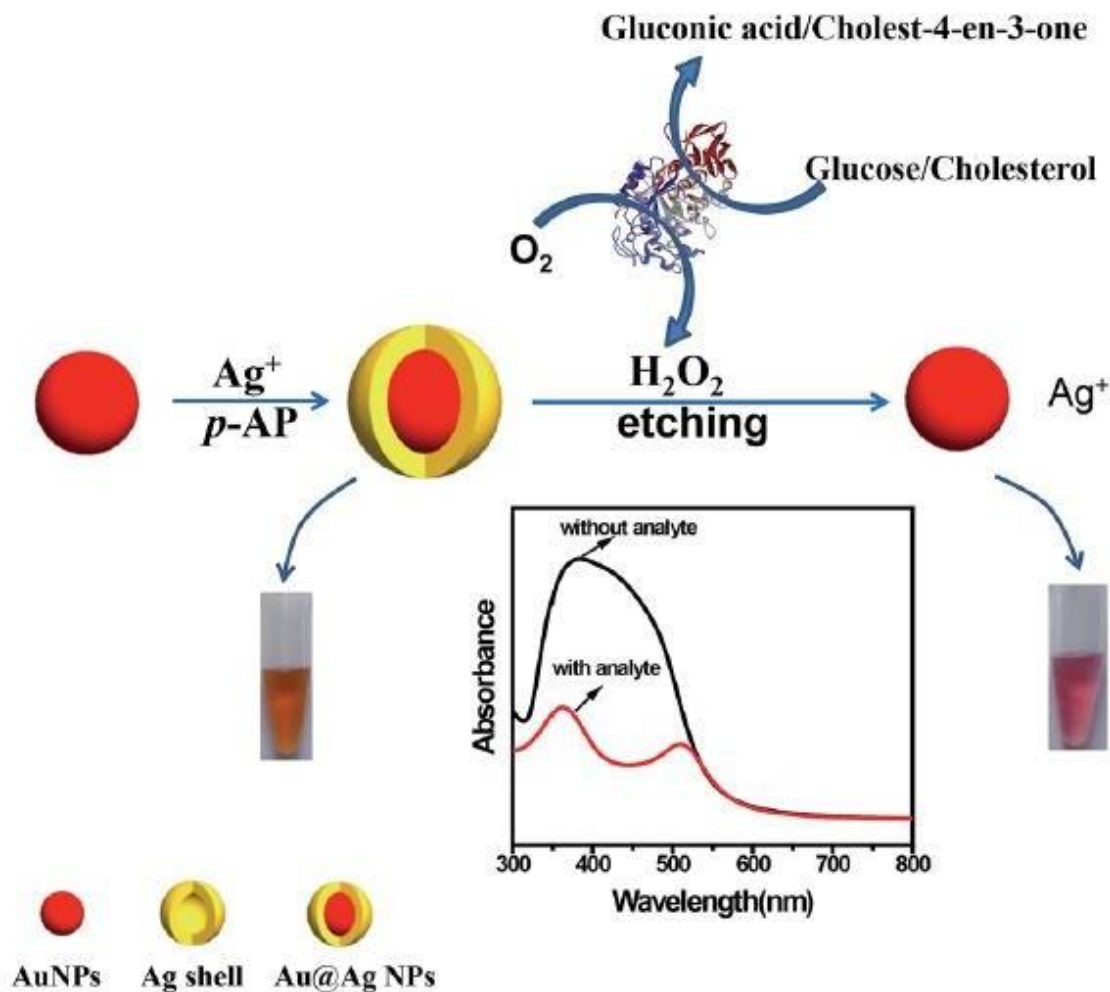
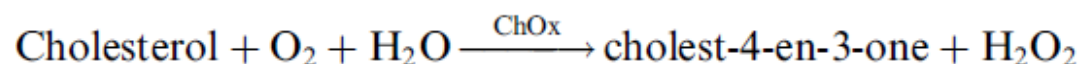
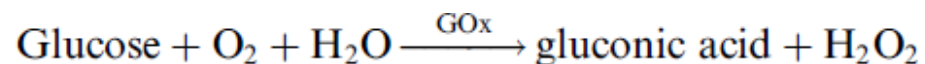
# Metal nanoparticles etching

## Etching phenomena study. $\text{H}_2\text{O}_2$ determination



# Metal nanoparticles etching

## Glucose and cholesterol evaluation through MNPs etching



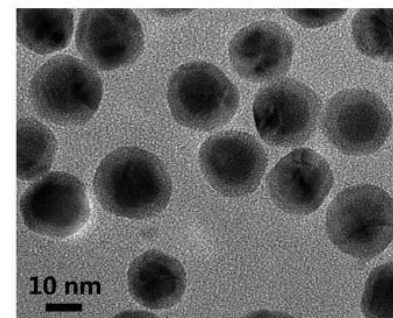
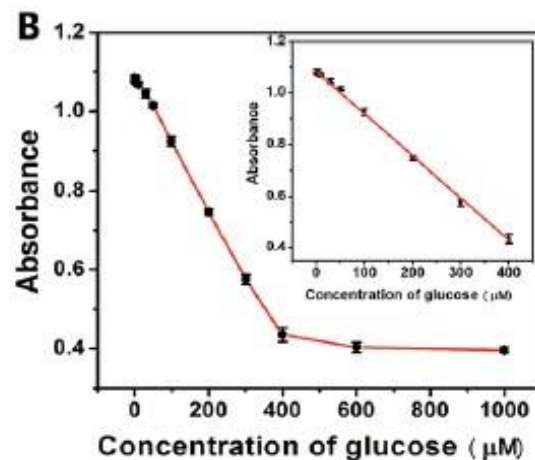
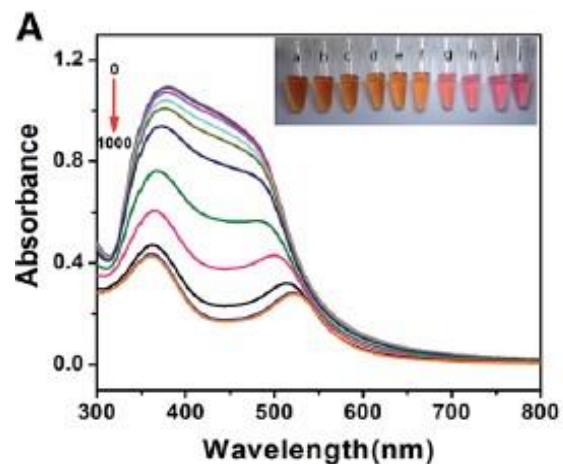
Scheme 1 Schematic illustration of the formation of Au@Ag NPs and its application for the colorimetric detection of  $\text{H}_2\text{O}_2$  and glucose/cholesterol.



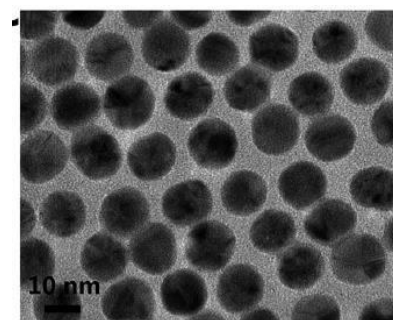
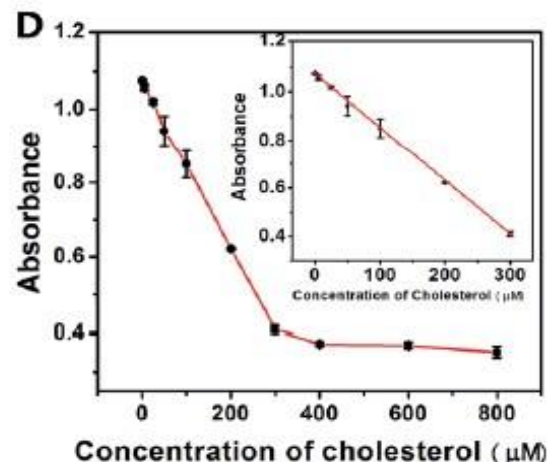
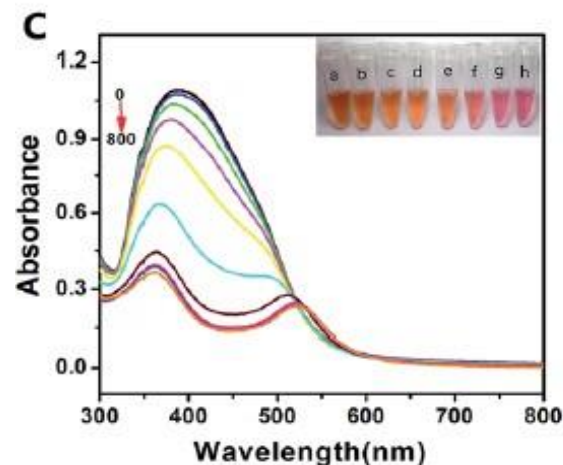
# Metal nanoparticles etching

## Glucose and cholesterol determination through MNPs etching

### Dose-response curve



Etching



### Recovery study

**Table 1** Recovery measurements of glucose in human urine samples and free cholesterol in human serum samples

Analytes	Spiked (mM)	Found (mM)	Recovery (%)	RSD (%) (n = 3)
Glucose	0	0.580	—	0.84
	1	1.552	97.2	0.51
	5	5.530	99.0	1.02
	10	11.041	104.6	2.66
	30	31.037	101.5	3.83
Cholesterol	0	1.544	—	0.90
	1	2.610	106.6	0.43
	5	6.320	95.6	2.69
	10	11.715	101.7	1.88
	30	31.283	99.1	5.88

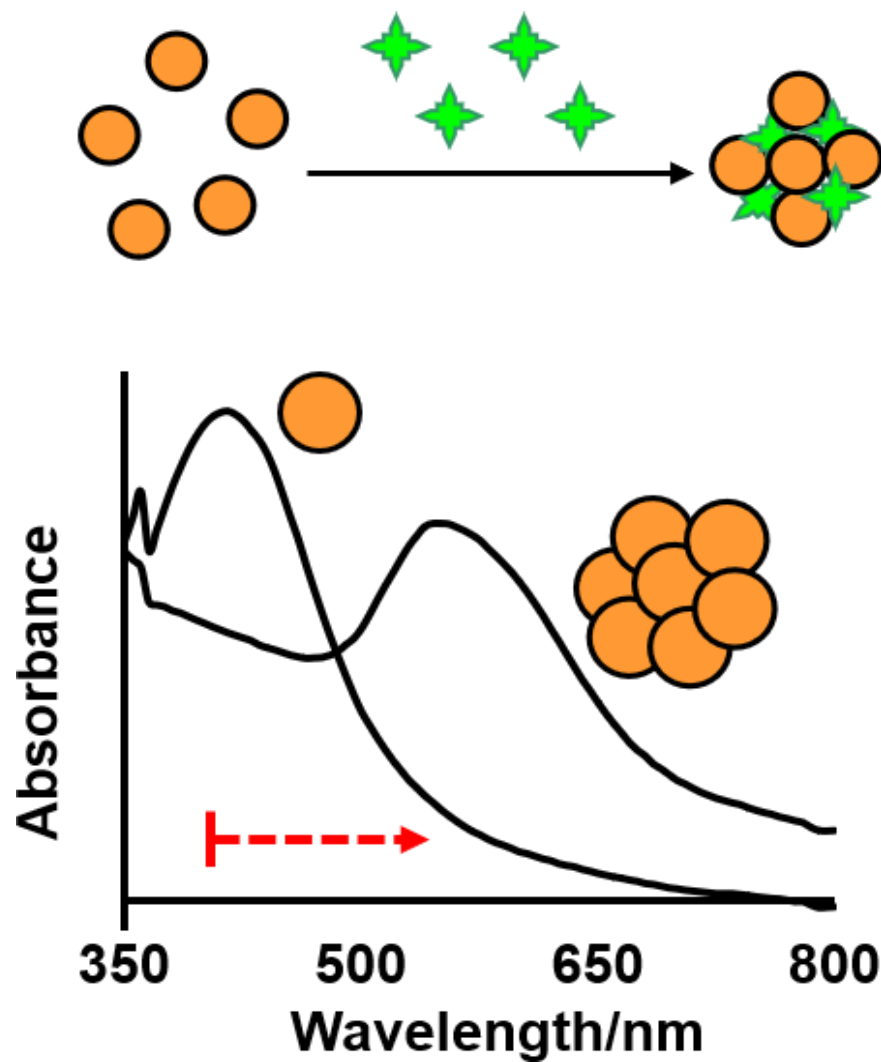
### Sample analysis

**Table 2** Determination of glucose concentration in human serum samples

Sample	This work (mM)	RSD (%) (n = 3)	Glucometer (mM)	RSD (%) (n = 3)
1	4.83	2.69	4.70	4.26
2	7.30	4.46	7.53	3.34
3	8.79	4.82	8.97	1.70
4	10.36	3.09	10.23	2.46

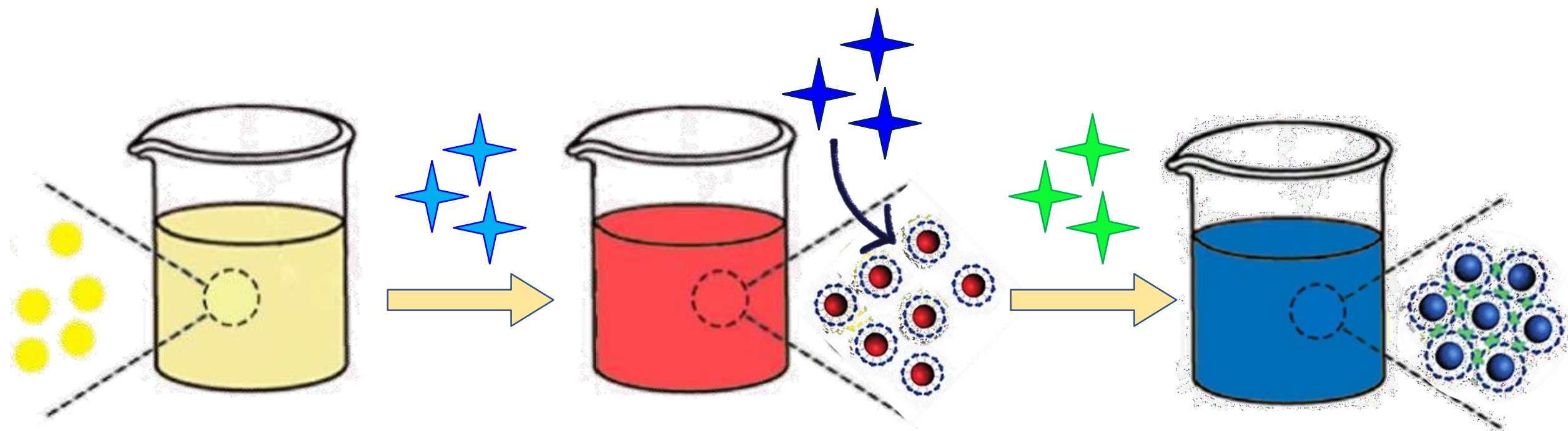


## Metal nanoparticle aggregation



# Metal nanoparticles aggregation

## Main strategy



● Metal salts

★ Reductant

● MNPs

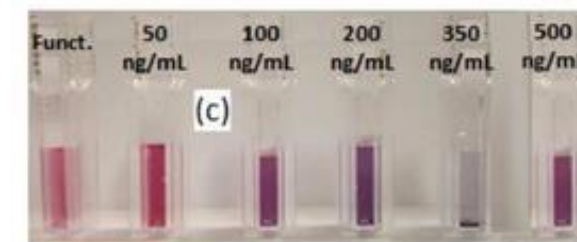
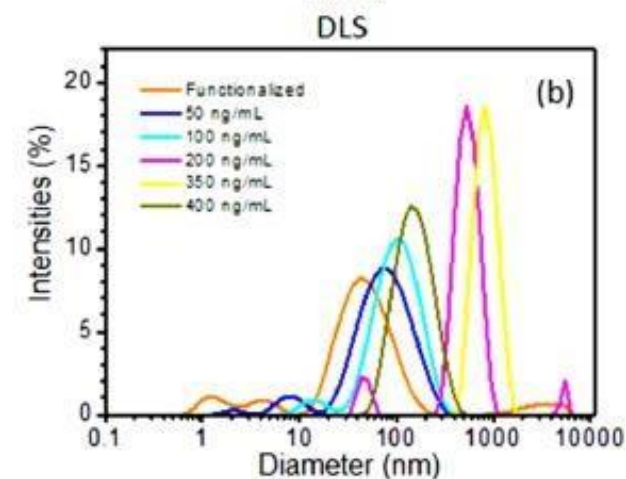
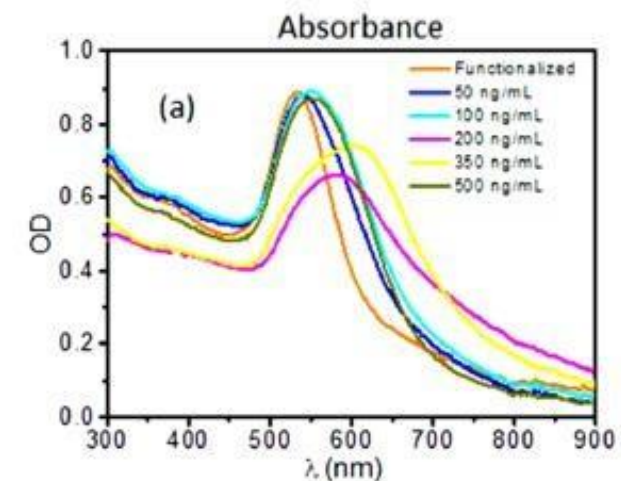
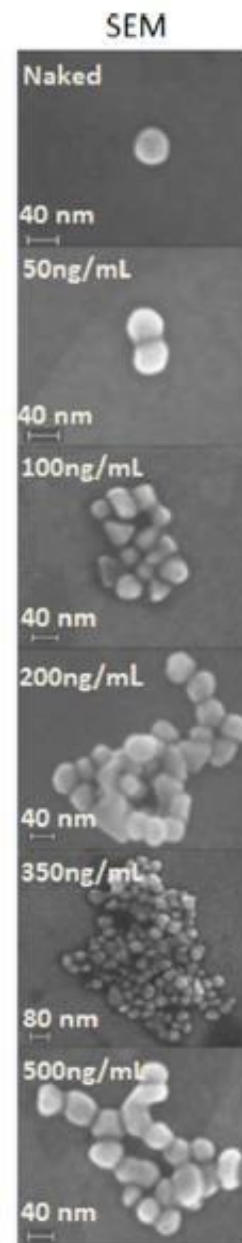
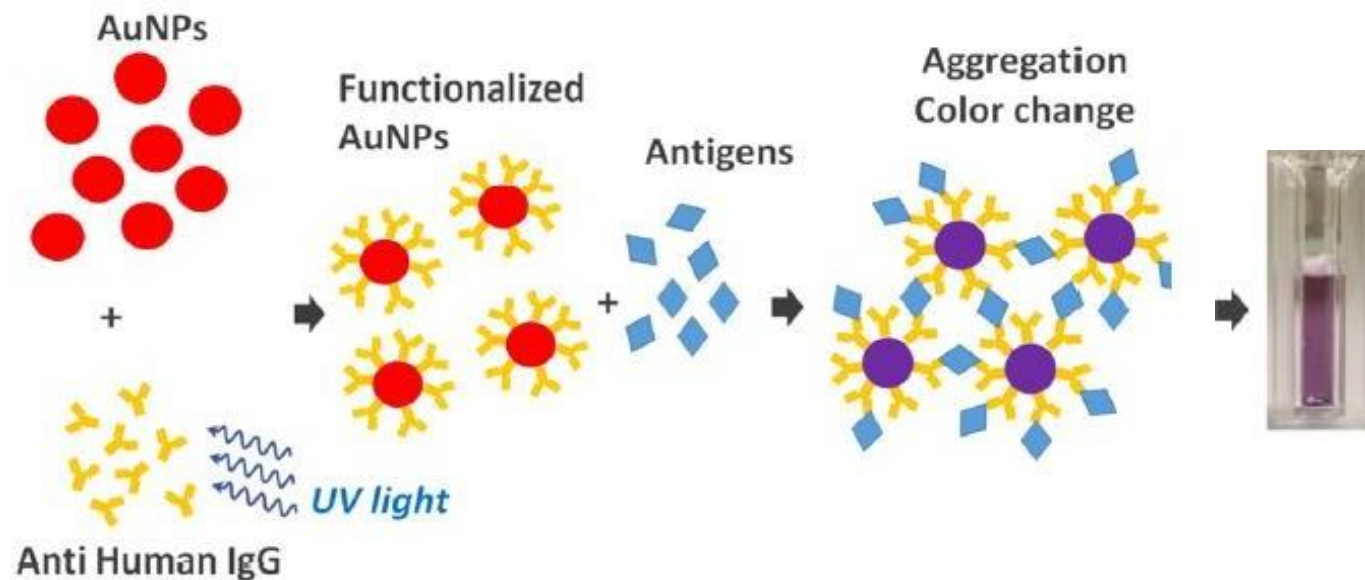
★ Functionalization

★ Analytes

● Aggregated MNPs

# Metal nanoparticles aggregation

## Immuno-based determination of HIgG



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Article

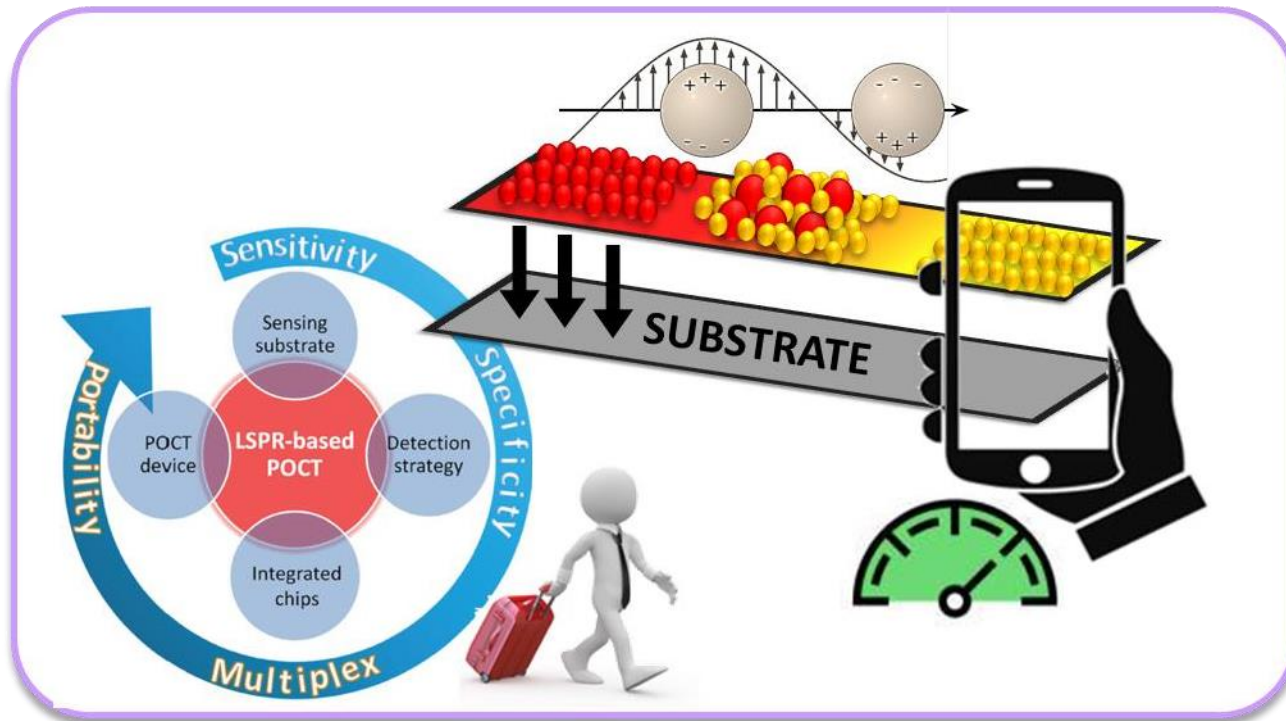
Cite This: ACS Omega 2018, 3, 3805–3812



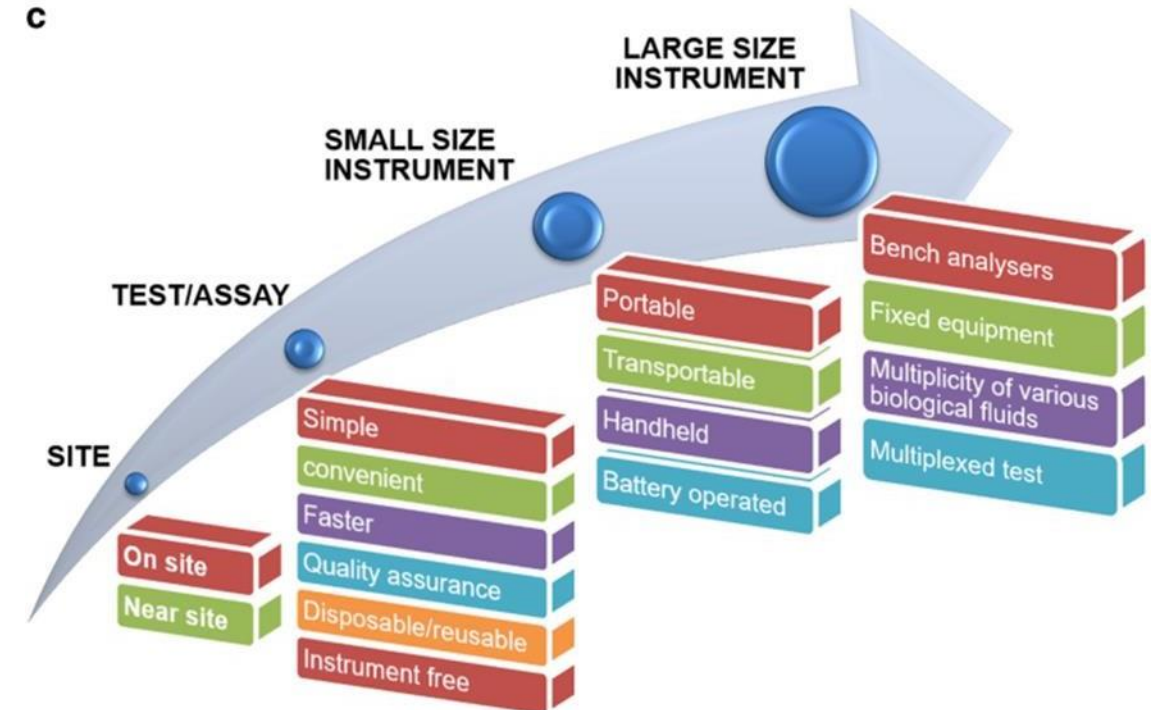
### Colorimetric Immunosensor by Aggregation of Photochemically Functionalized Gold Nanoparticles

Marzia Iarossi,<sup>†,||</sup> Chiara Schiattarella,<sup>†,‡</sup> Ilaria Rea,<sup>‡</sup> Luca De Stefano,<sup>‡</sup> Rosalba Fittipaldi,<sup>§</sup> Antonio Vecchione,<sup>§</sup> Raffaele Velotta,<sup>\*,†,||</sup> and Bartolomeo Della Ventura<sup>†</sup>





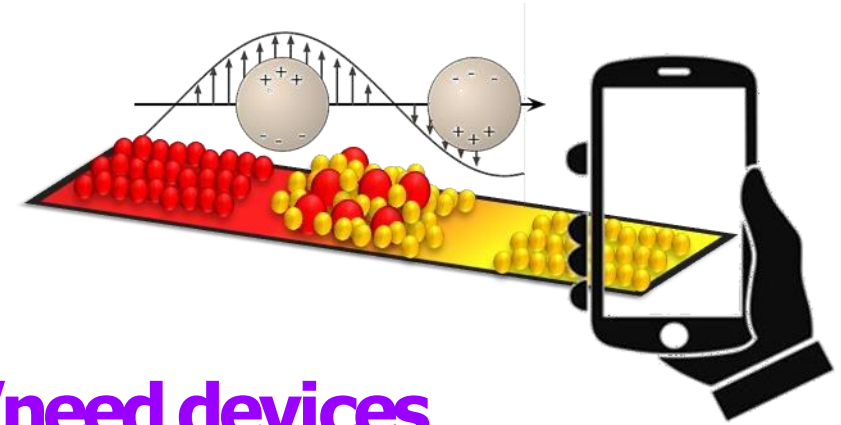
**!!! Lab-on-a-strip  
Device !!!**





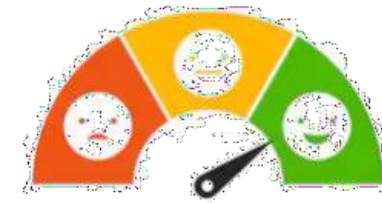
# Metal nanoparticles integration onto solid substrates

Main Point of Care and Point On Needs device requirements



## Point of care/need devices

**A**ffordable  
**S**ensitive  
**S**pecific  
**U**ser friendly  
**2x R**apid & robust  
**E**quipment-free  
**D**elivered

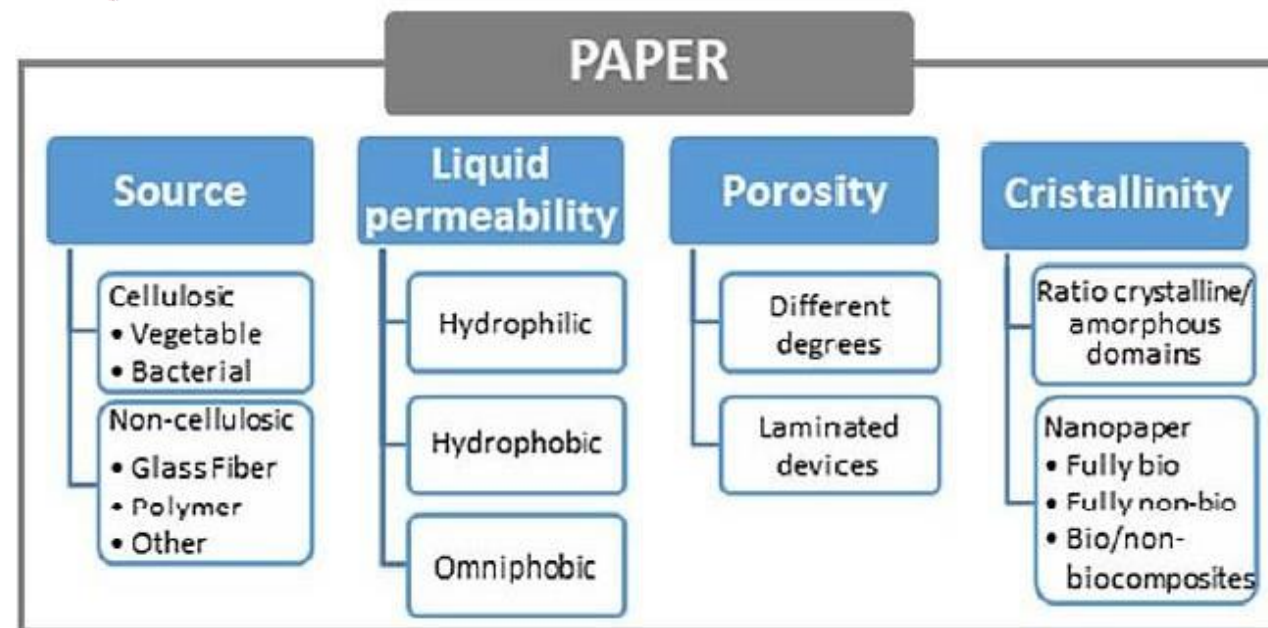
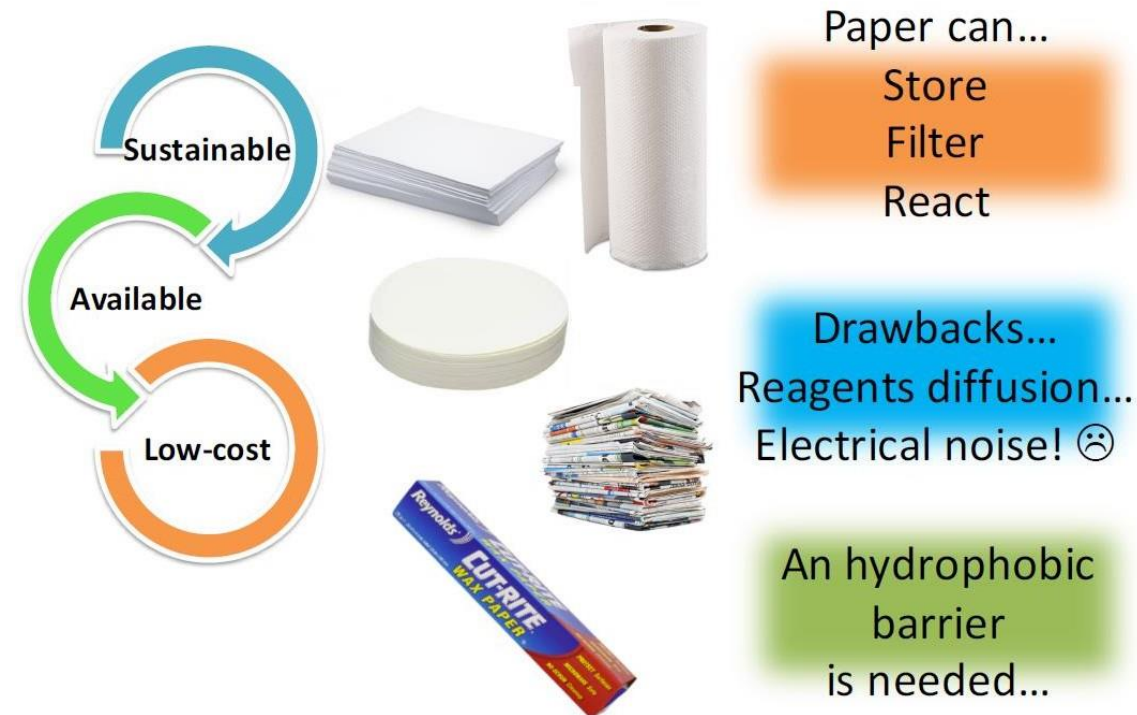


Cost performance

Manufacturing

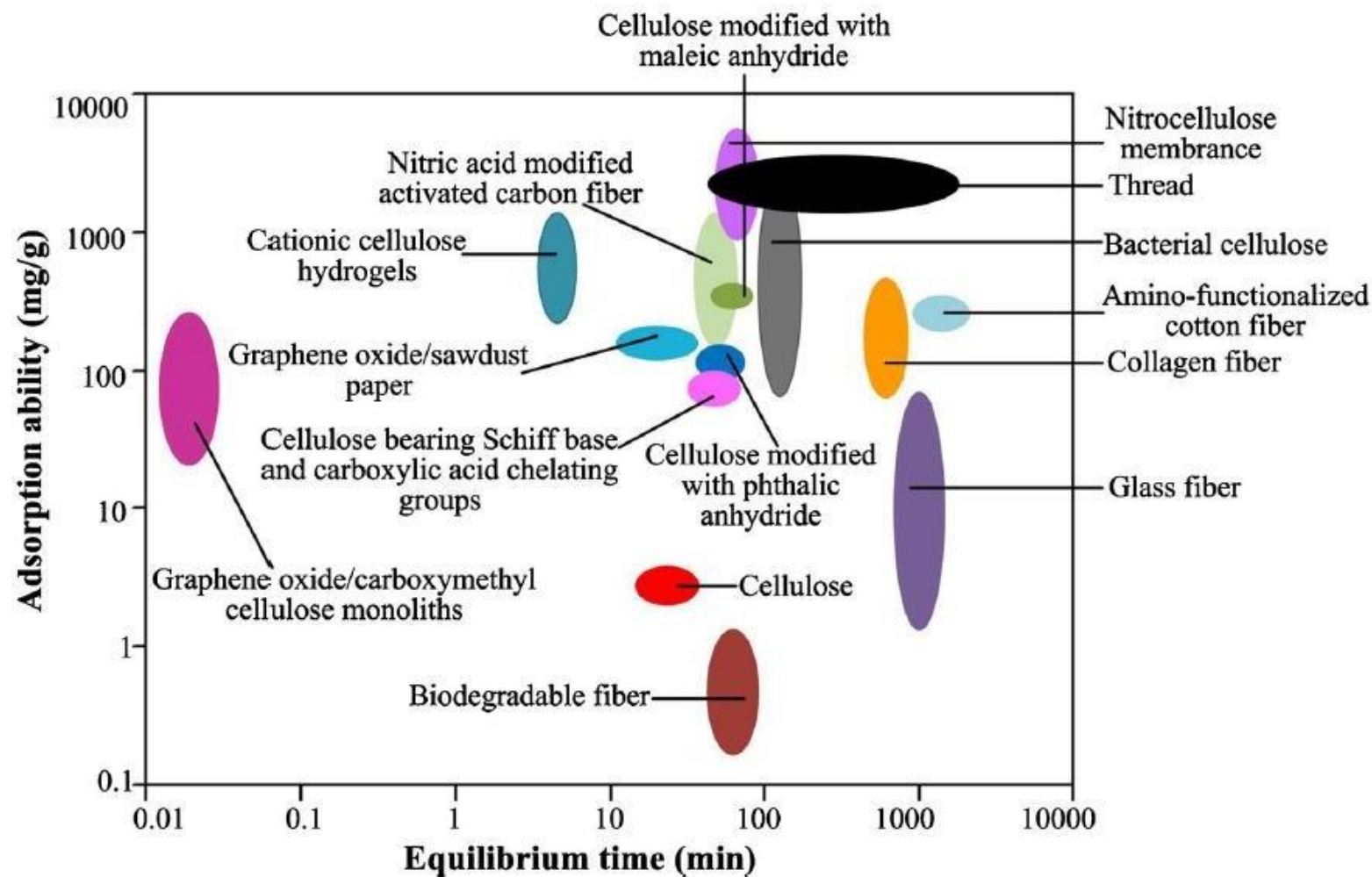
Mass production

## Paper as substrate



# Paper as elective substrate

## Kind of paper based substrates





# Paper as elective substrate

## Paper can be tailored

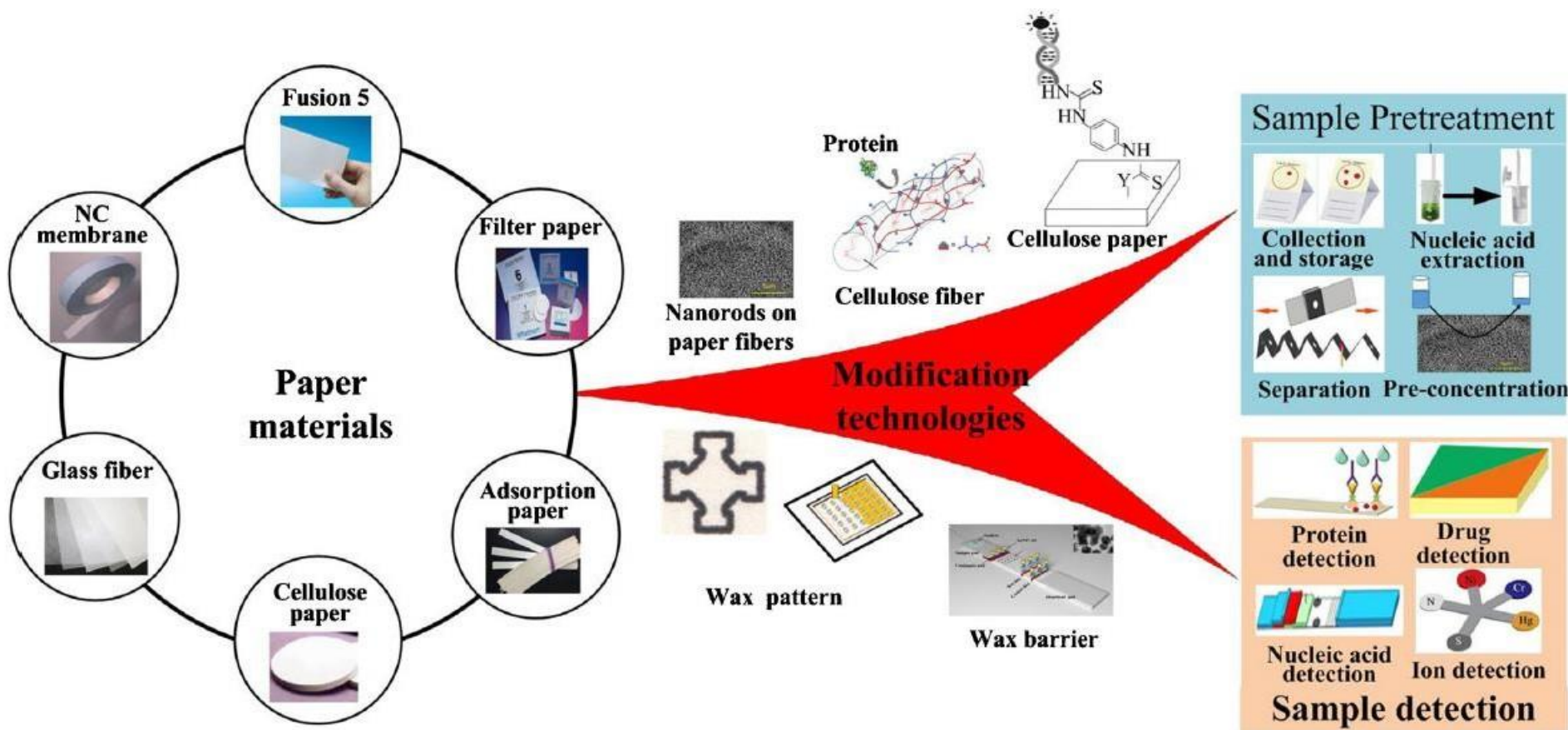


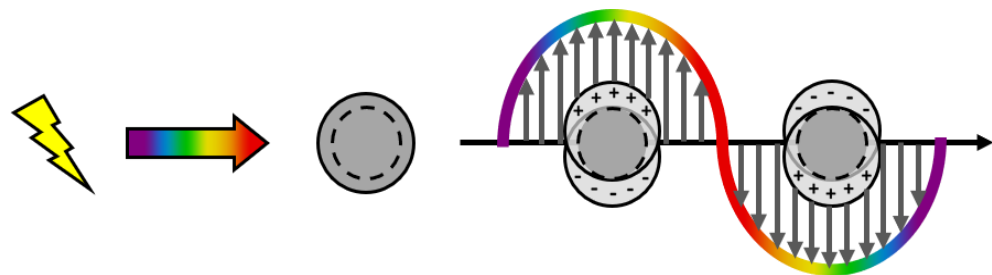
Fig. 1 Existing paper modification approaches for paper-based POCT. Different paper materials, including Fusion 5, filter paper, chromatography paper, cellulose paper, Whatman® No.1 filter paper and NC

membrane, have been modified with various reagents for paper-based sample pretreatment and paper-based detection

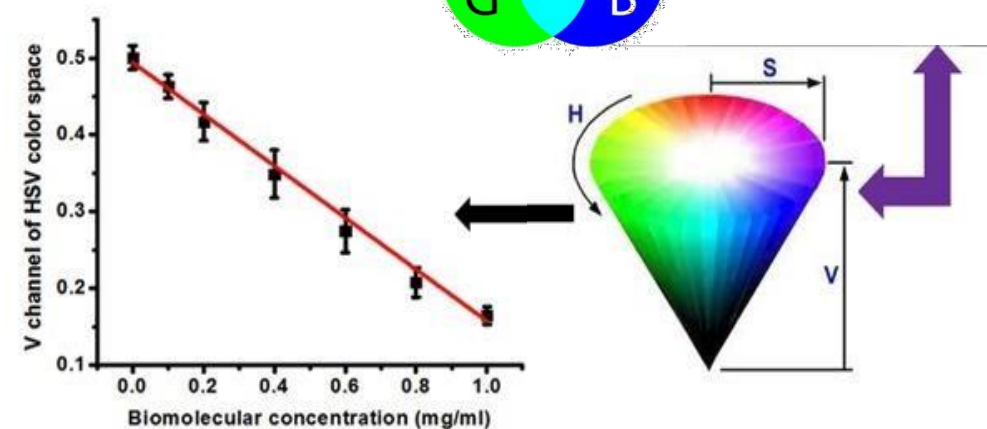
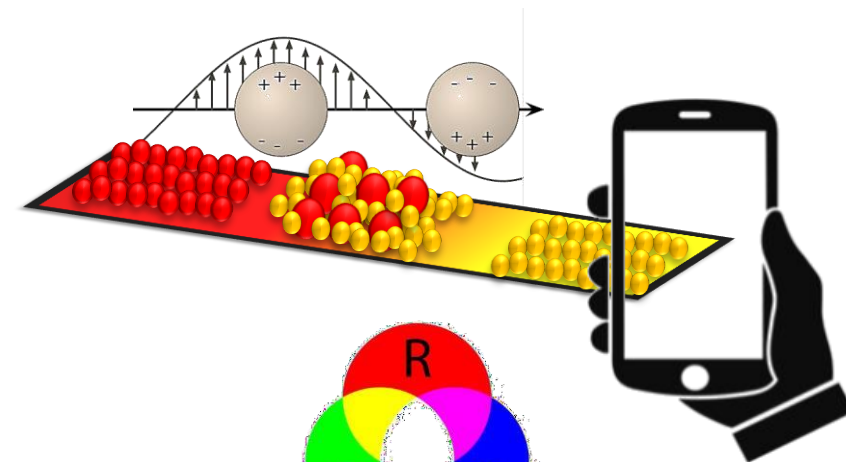
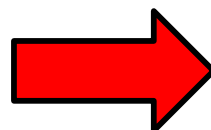
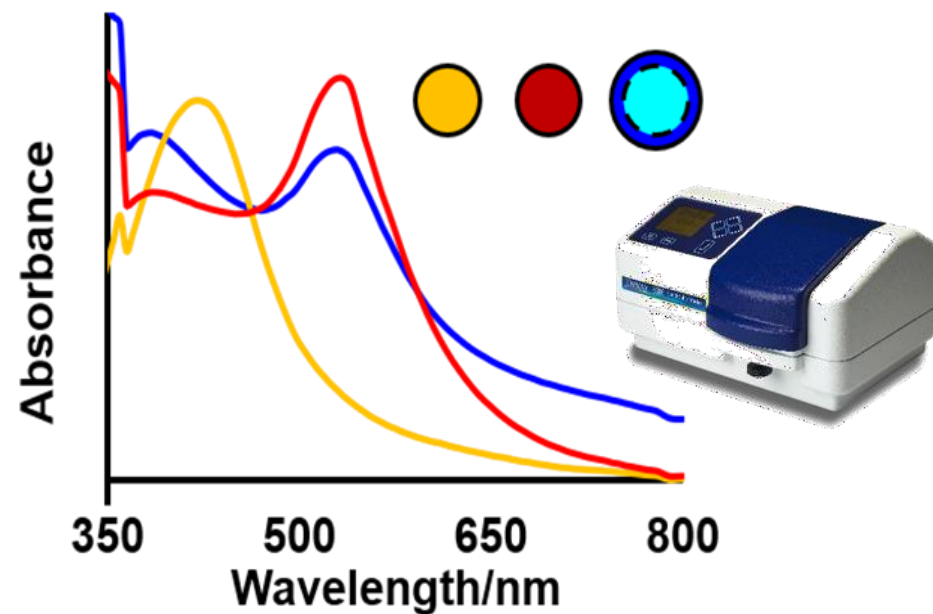


# Paper as elective substrate

## From plasmonic... Towards colorimetric strategies

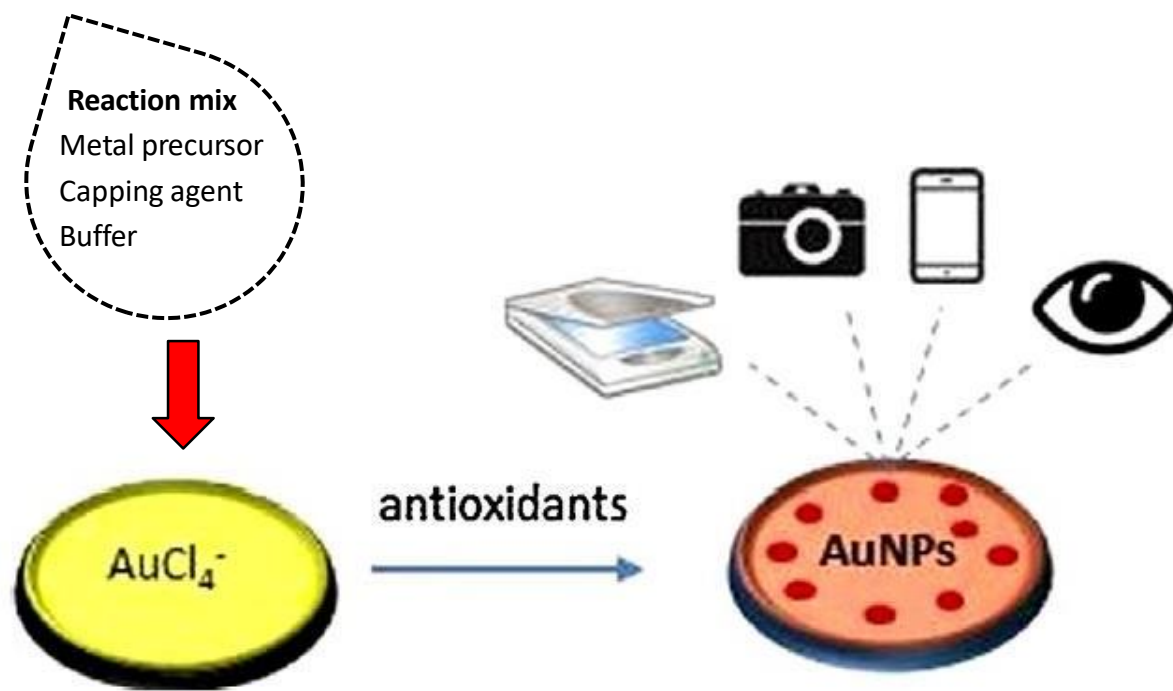


### Localized Surface Plasmon Resonance



# Paper-based colorimetric sensor

## Phenolic content and antioxidant capacity evaluation through AuNPs formation



Dose-response curve

Catechin



Gallic acid



Caffeic acid



Ascorbic acid



Goimanic acid



Vanillic acid



Ferullic acid



Cinnamic acid



Analytica Chimica Acta 860 (2015) 61–69

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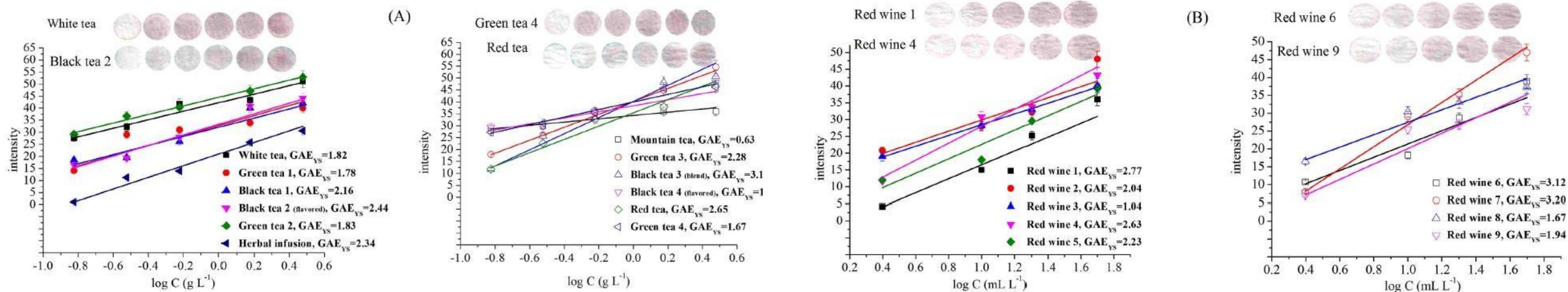
Paper-based assay of antioxidant activity using analyte-mediated on-paper nucleation of gold nanoparticles as colorimetric probes

Tatiana G. Choleva, Foteini A. Kappi, Dimosthenis L. Giokas\*, Athanasios G. Vlessidis

# Paper-based colorimetric sensor

## Phenolic content and antioxidant capacity evaluation through AuNPs formation

### Sample dose-response curve



### Sample analysis

Evaluation of antioxidant activity of commercial teas by the Au-AuNP paper sensor and comparison with conventional assays. RSD range between 2.9 and 14.4%.

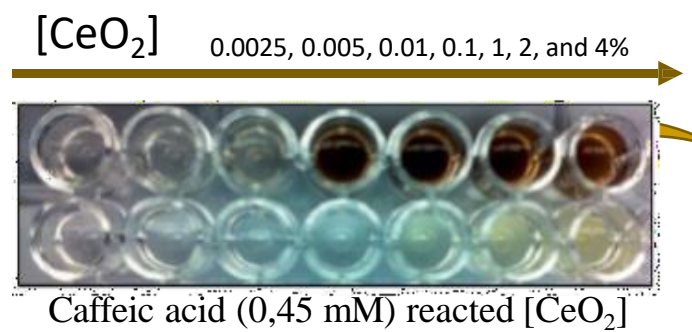
Tea sample	Au sensor Antioxidant activity (mg catechin g <sup>-1</sup> )	Au sensor Antioxidant activity (mg gallic acid g <sup>-1</sup> )	Folin-Ciocalteu Total phenolic content (mg gallic acid g <sup>-1</sup> )	CUPRAC Total antioxidant activity (mg Trolox g <sup>-1</sup> )	Aluminum assay Total flavonoid content (mg catechin g <sup>-1</sup> )
White tea	59.49	6.52	91.00	196.54	31.63
Green tea 1	56.81	5.76	95.30	208.61	26.76
Black tea 1	39.09	2.10	42.46	95.01	15.06
Black tea 2 (flavored)	24.26	0.58	52.72	114.28	18.47
Green tea 2	59.19	6.43	100.83	232.42	31.63
Herbal infusion	14.27	0.14	33.58	67.04	16.04
Mountain tea	60.44	6.80	31.54	67.83	21.88
Green tea 3	89.78	19.80	79.43	180.87	24.32
Black tea 3 (blend)	55.86	5.50	41.44	97.52	16.52
Black tea 4 (flavored)	44.12	2.91	69.83	147.97	23.35
Red tea	38.03	1.95	52.29	119.45	22.37
Green tea 4	120.60	43.93	107.53	231.87	60.87



# Paper-based colorimetric sensor

## Phenolic content and antioxidant capacity evaluation through NanoCeria formation

### Optimization



[CeO<sub>2</sub>] = 4%

Analyst

RSC Publishing

PAPER

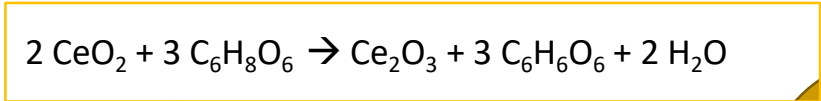
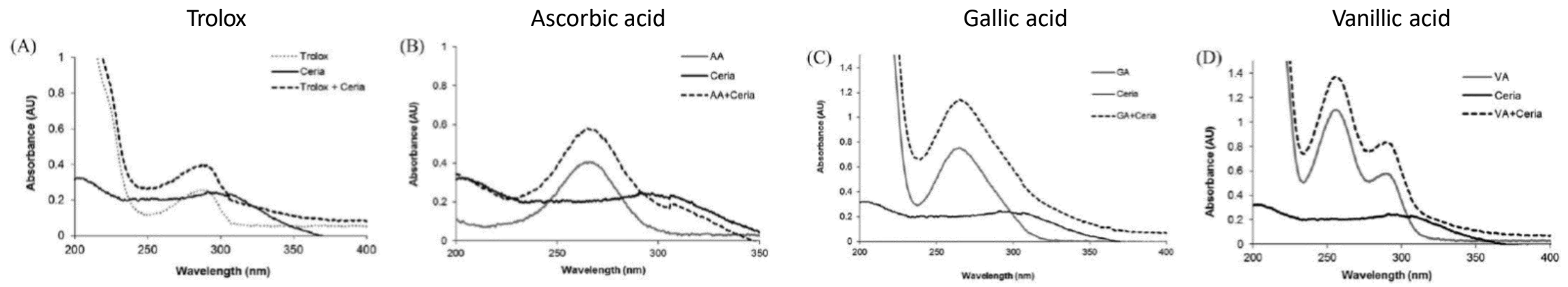
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View Journal

One this DOI: 10.1039/c2an36205h

Portable ceria nanoparticle-based assay for rapid detection of food antioxidants (NanoCeraC)

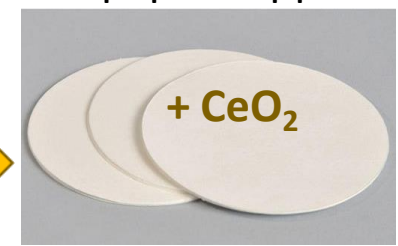
Erica Sharpe, Thalia Frasco, Daniel Andreescu and Silvana Andreescu\*

Uv-vis spectra of ceria nanoparticles dispersion (13 ppm) in the presence and absence of selected antioxidants.



From dispersed system

to paper support

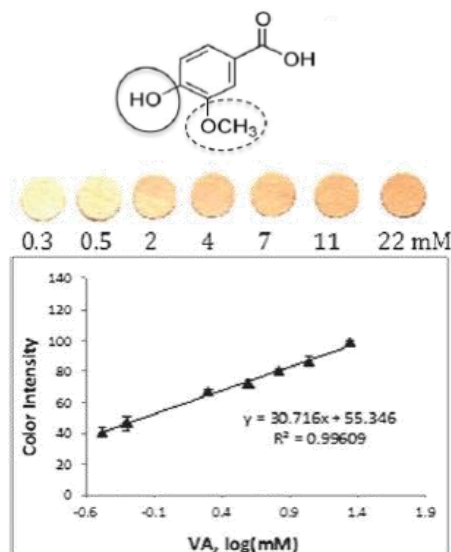
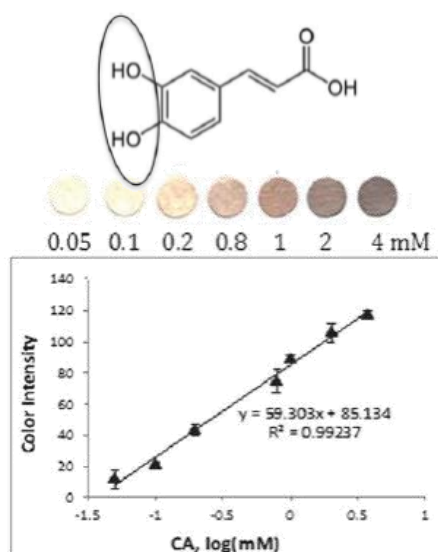
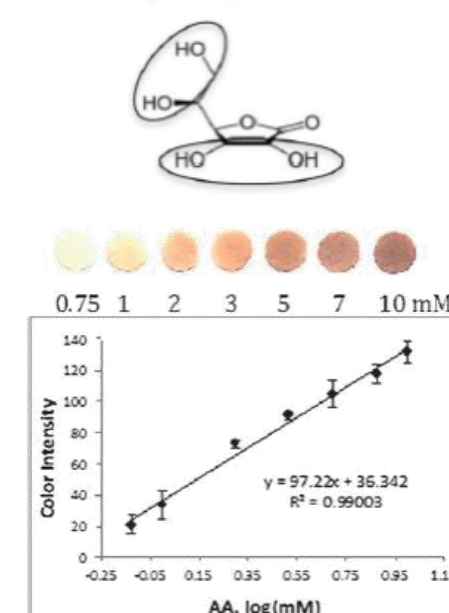
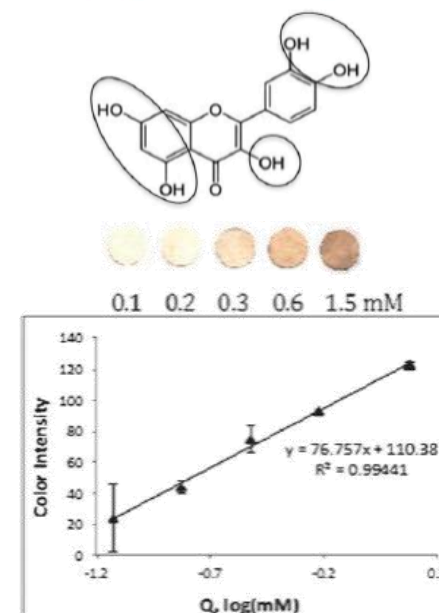
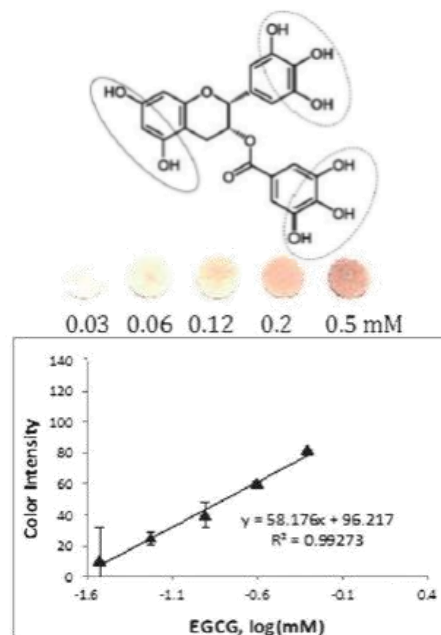
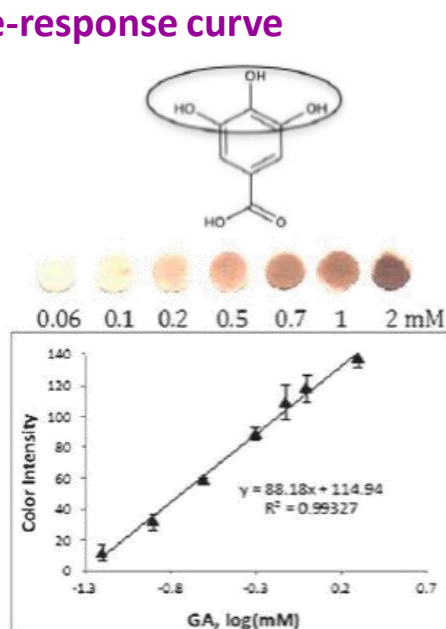




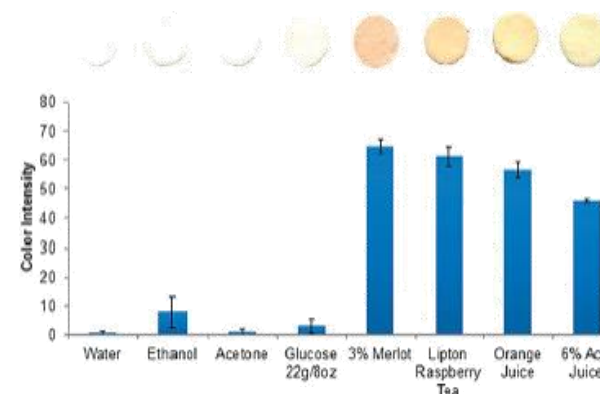
# Paper-based colorimetric sensor

## Phenolic content and antioxidant capacity evaluation through NanoCeria formation

### Dose-response curve



### Interferents evaluation



### Tested interfering compounds

Common lab solvent:

- water,
- ethanol,
- acetone

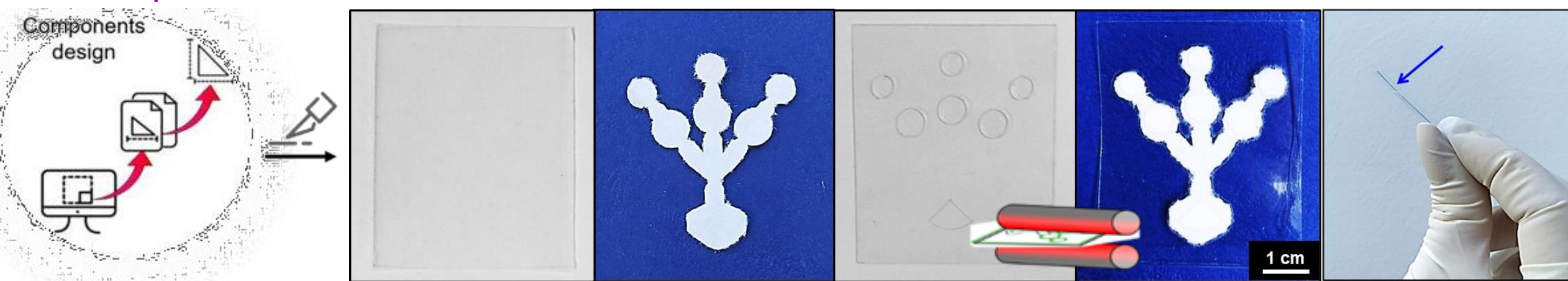
Common sugar presents in:

- juice,
- wine,
- commercial teas

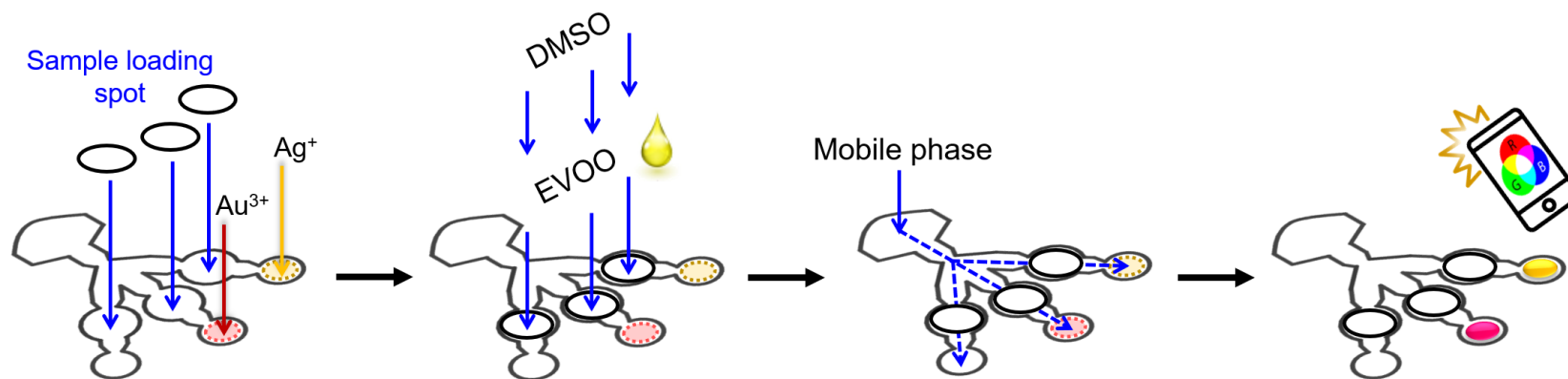
# Paper-based colorimetric sensor

## Extraction-free olive oil phenolic compounds evaluation through a seed growth strategy

### Lab-on-a-strip fabrication

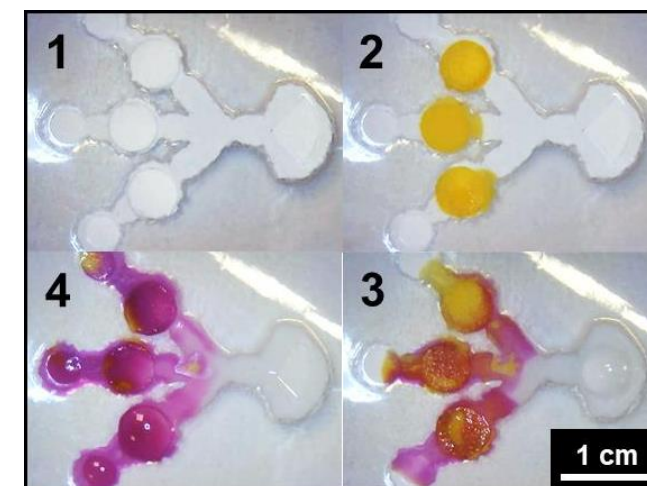


### Assay format



Total assay volume:  $\sim 80 \mu\text{L}$

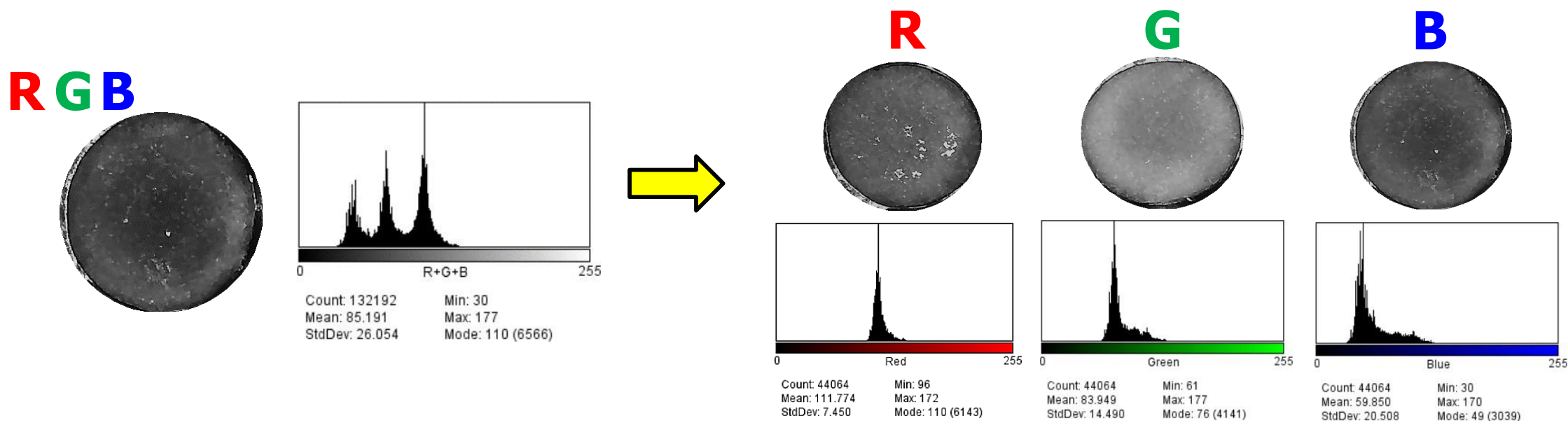
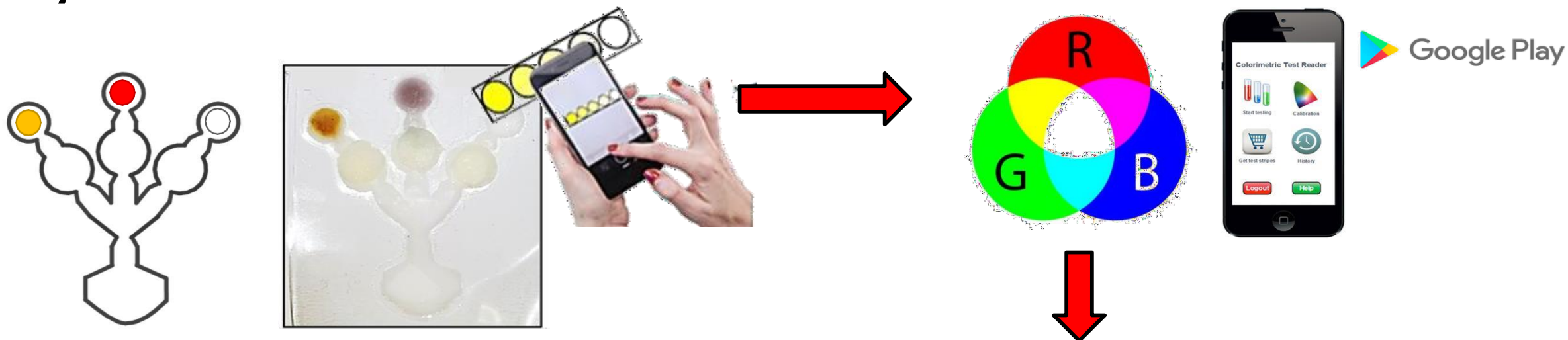
### Assay simulation with a colorimetric dye



# Paper-based colorimetric sensor

## Extraction-free olive oil phenolic compounds evaluation through a seed growth strategy

### Color analysis

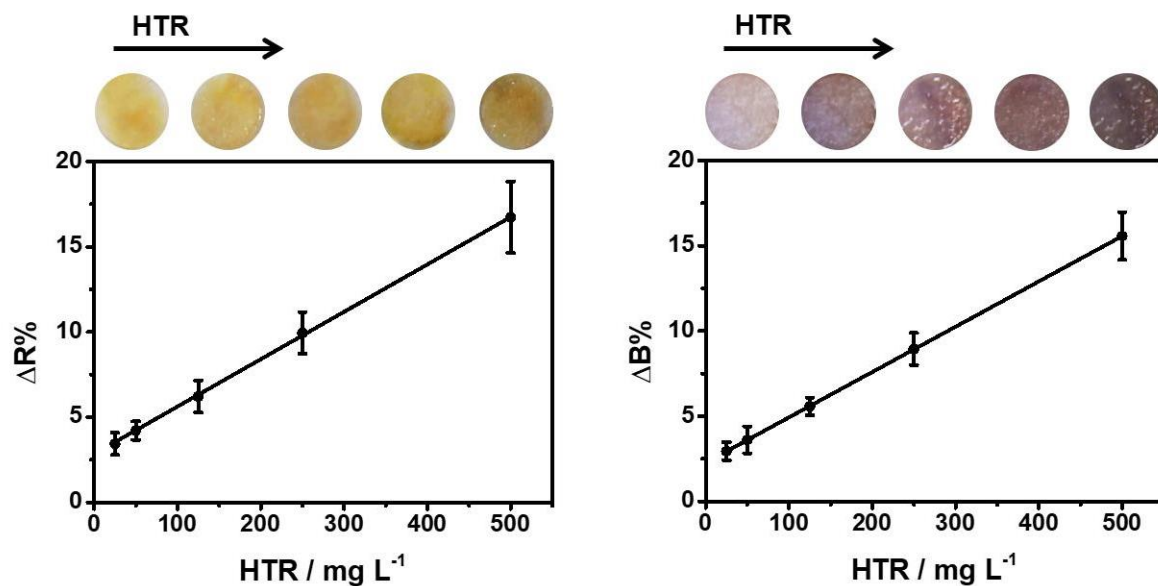




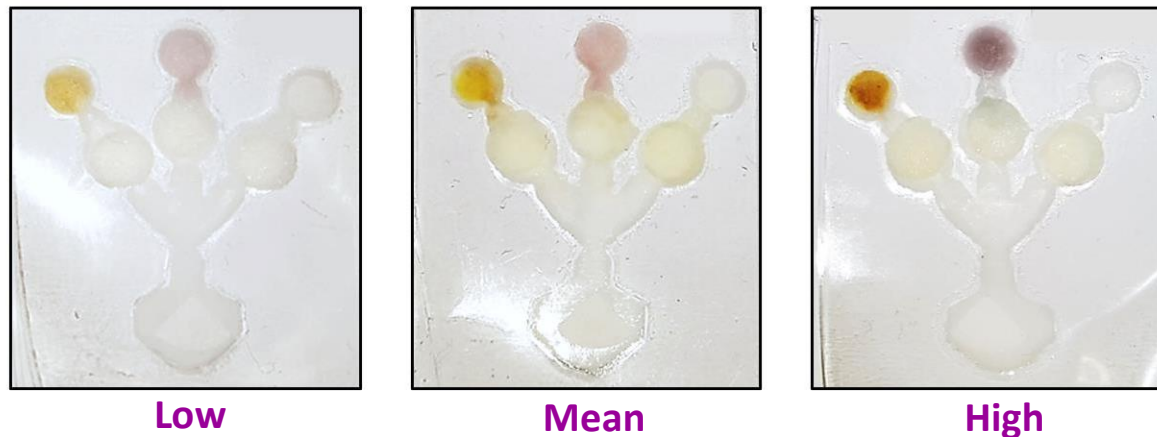
# Paper-based colorimetric sensor

## Extraction-free olive oil phenolic compounds evaluation through a seed growth strategy

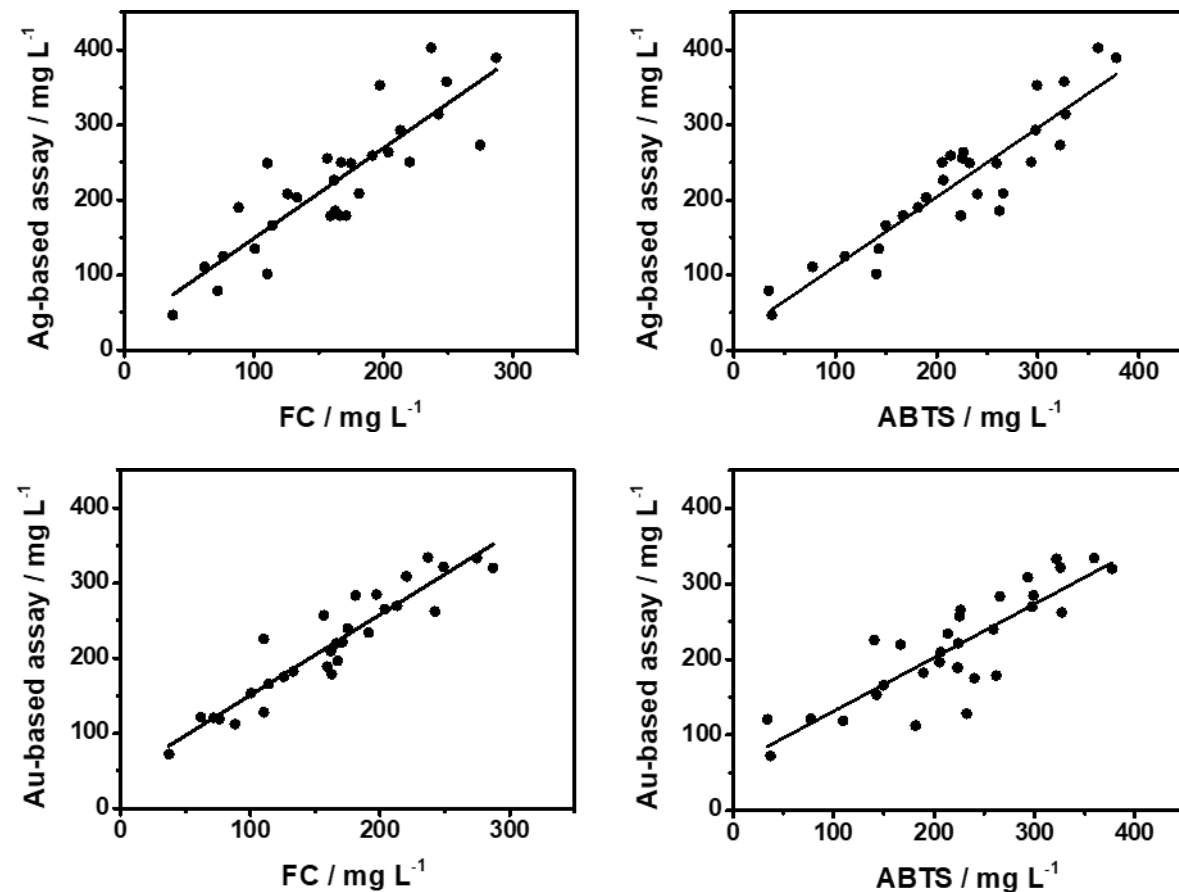
### Dose-response curve



### EVOO samples' phenolic compounds content



### Sample analysis, analytical performances

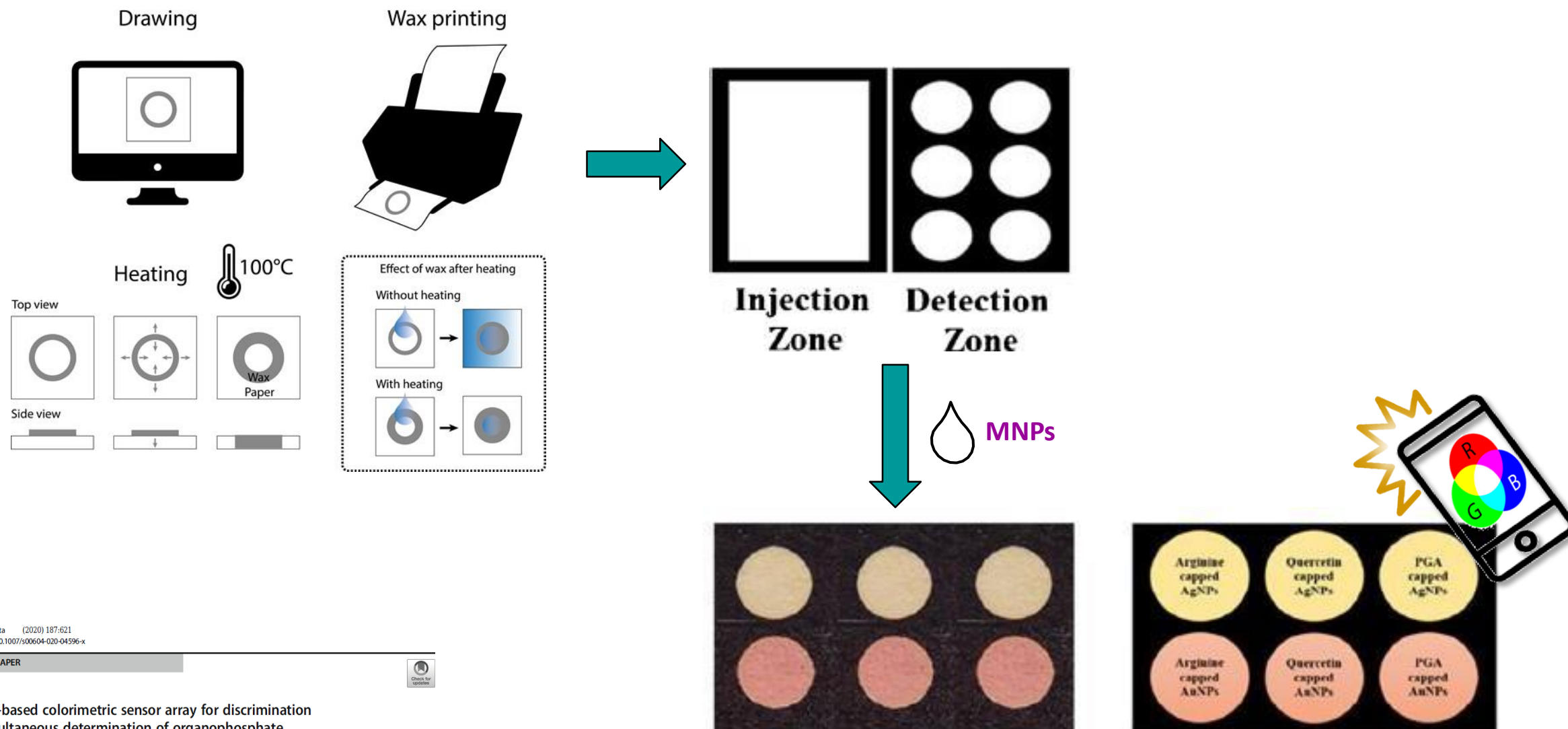


No interferences by compounds commonly present in EVOO



# Paper-based colorimetric sensor

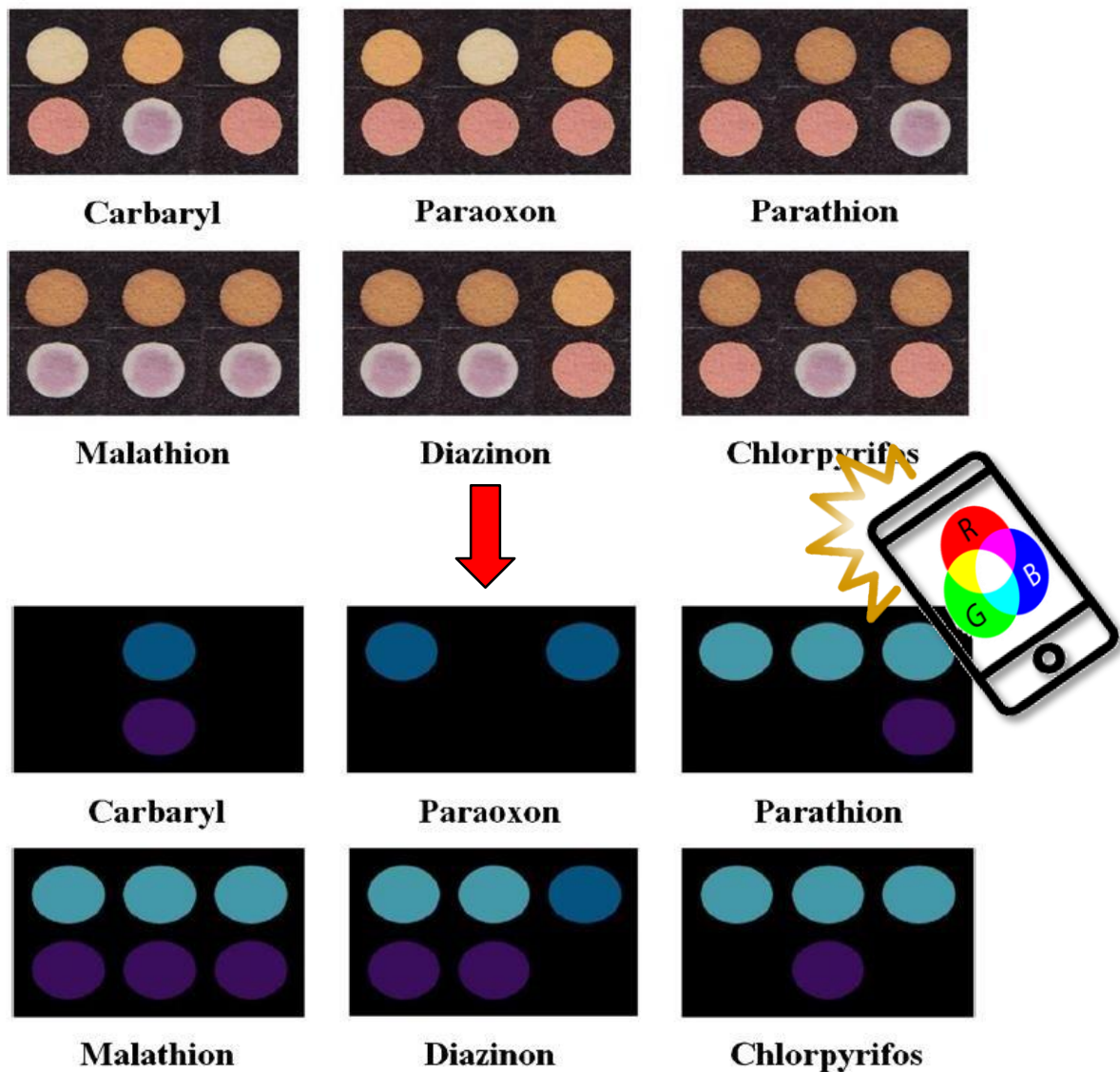
## Pesticides determination through MNPs aggregation integrated in a paper-based device



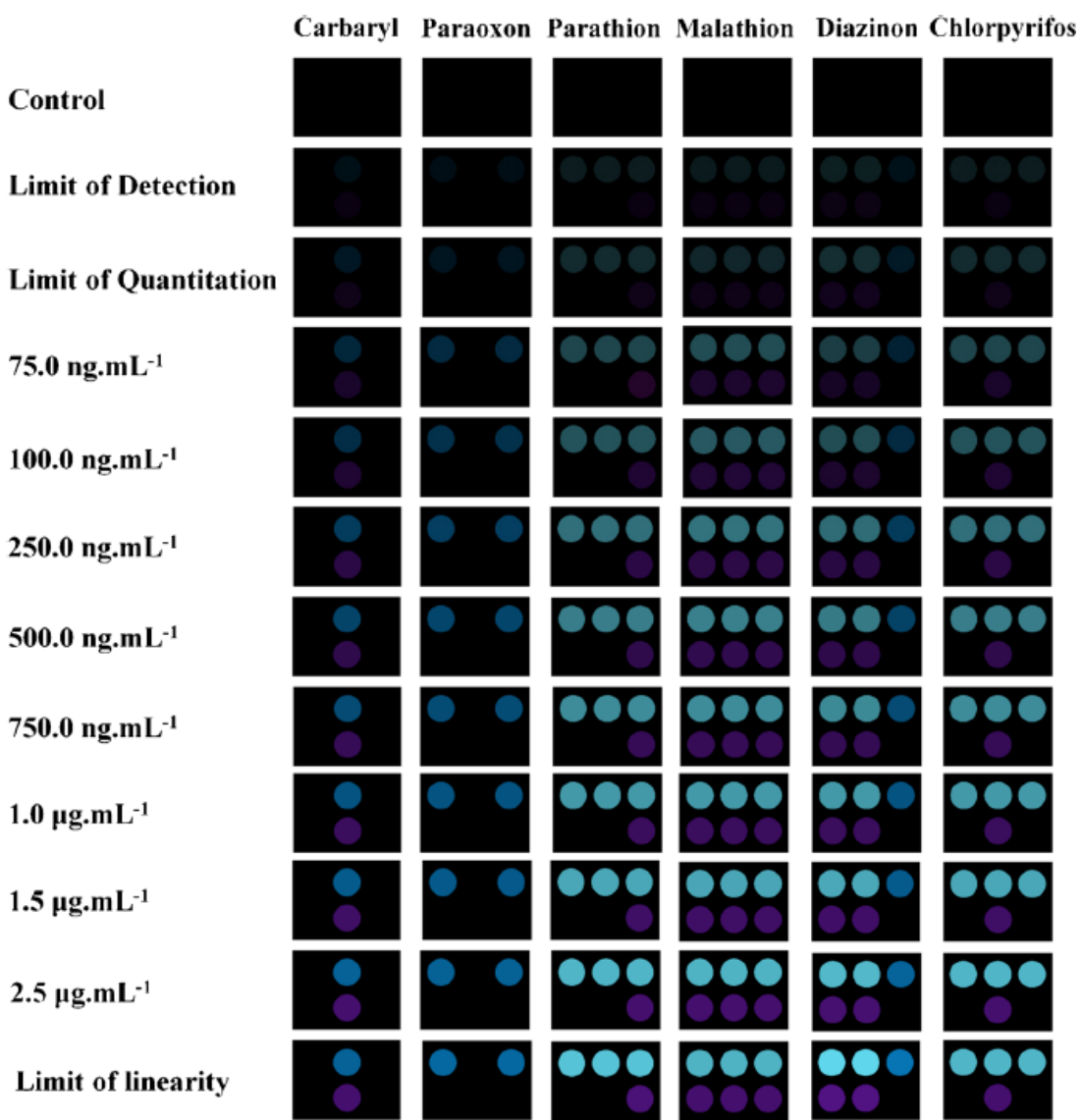
# Paper-based colorimetric sensor

## Pesticides determination trough MNPs aggregation integrated in a paper-based device

### Analytes screening

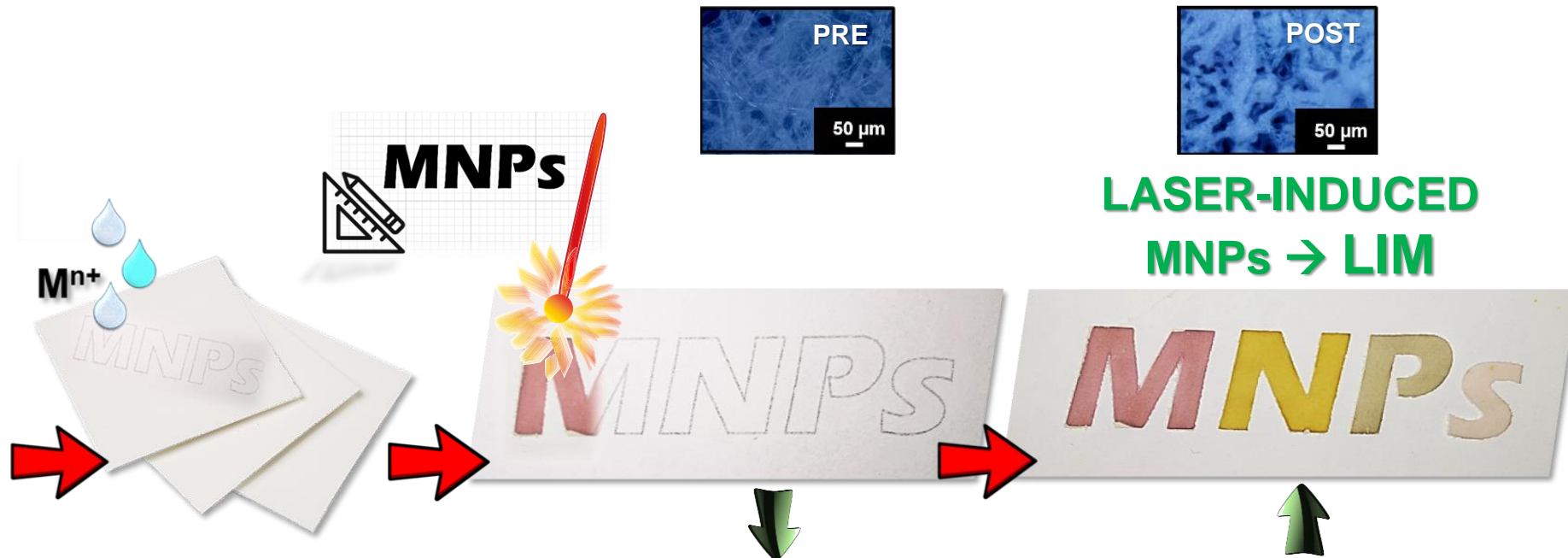
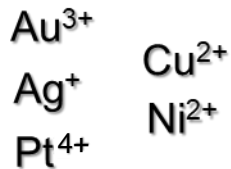
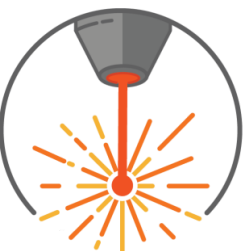


### Dose-response curve and analytical parameters

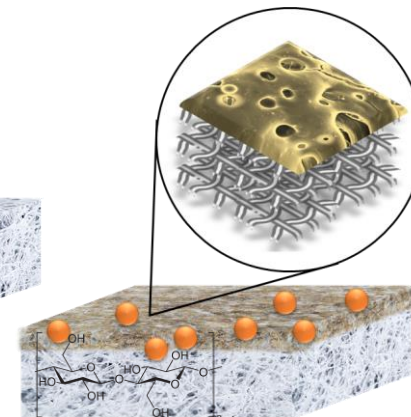
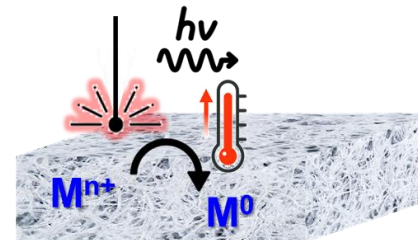
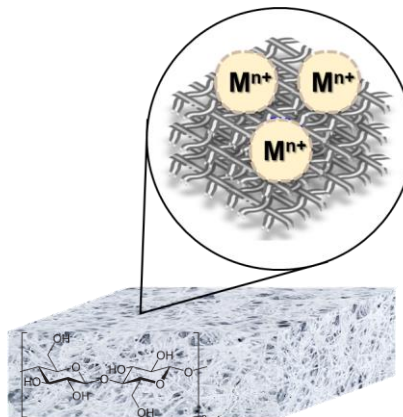
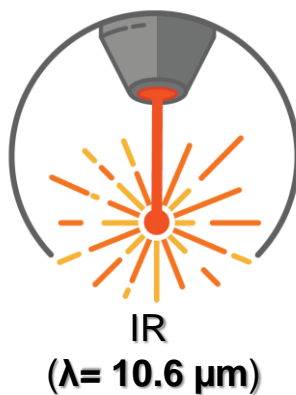


# Strategy: Laser-Induced Metal Nanoparticles (LIM)

**CO<sub>2</sub>-Laser**  
Plotter ( $\lambda = 10.6 \mu\text{m}$ )



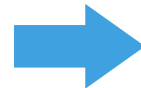
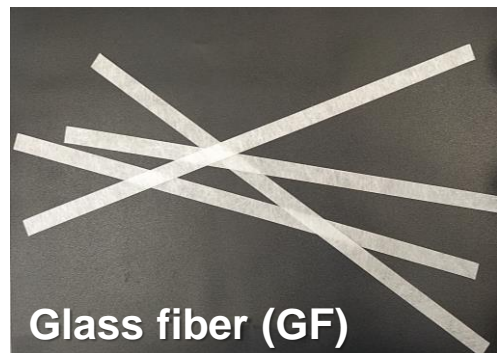
## FORMATION MECHANISMS



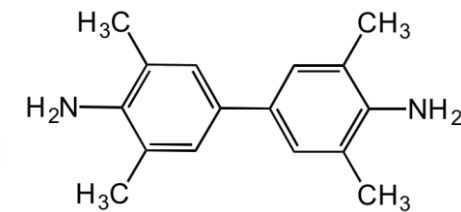
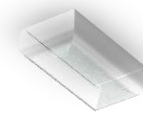
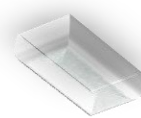


# LIM: Colorimetric determination of Ascorbic Acid

## Sensing layer: GF<sub>TMB</sub>



3,3',5,5'-Tetramethylbenzidine  
(TMB)



## Device manufacturing

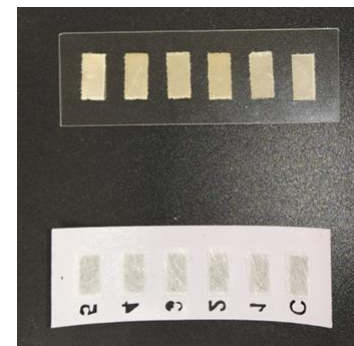
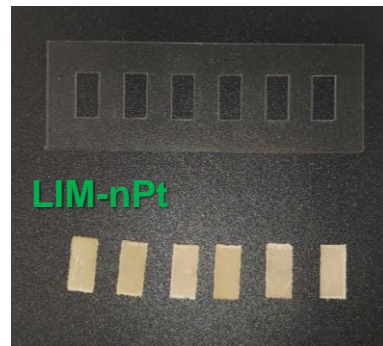
### 1) Modules fabrication

Cutting plotter

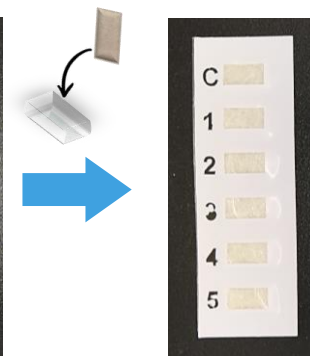


### 2) nanoCatalysts and Sensing layers assembling

Modules alignment



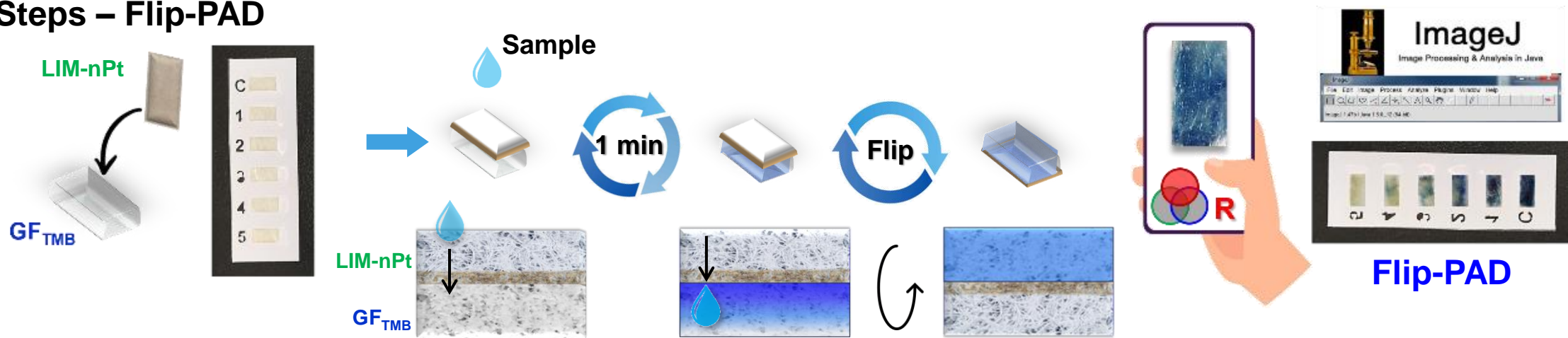
Modules assembling



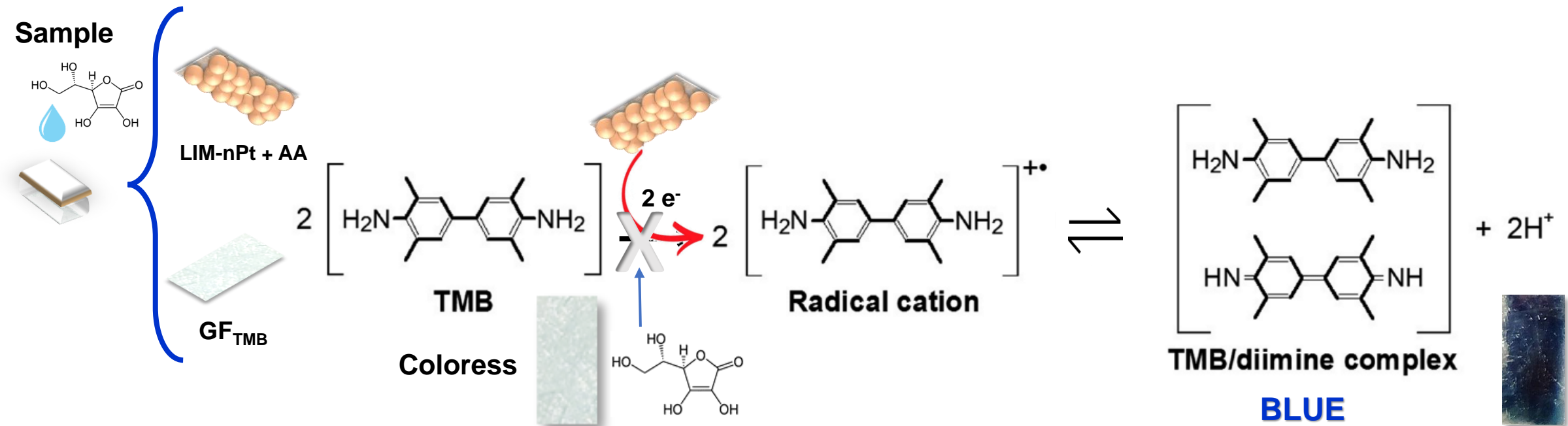


# LIM: Colorimetric determination of Ascorbic Acid

## Assay Steps – Flip-PAD

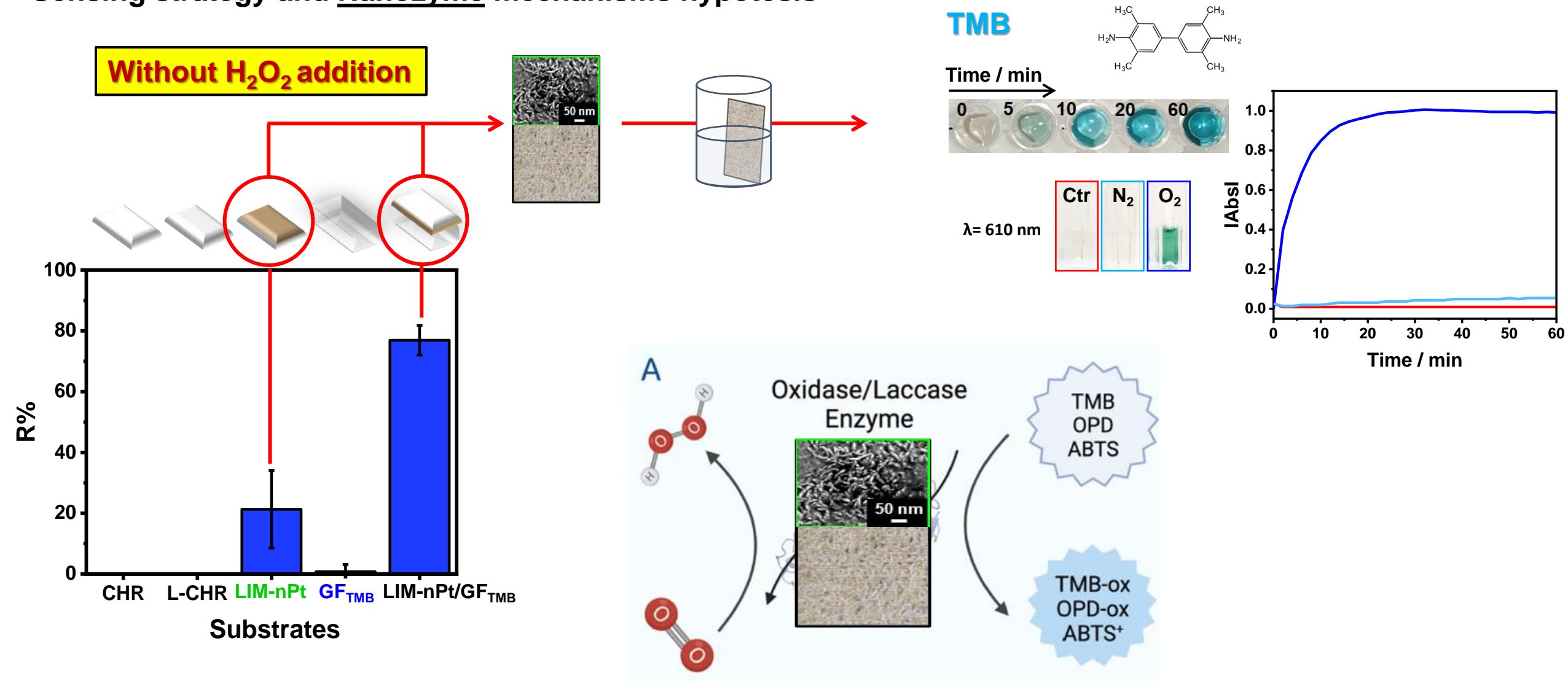


## Sensing strategy



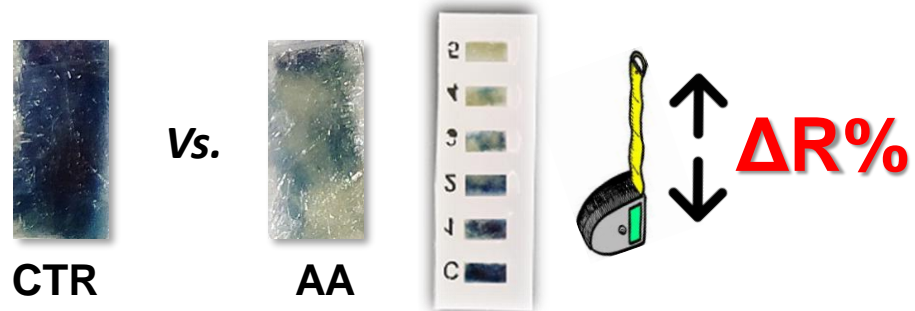
# LIM: Colorimetric determination of Ascorbic Acid

## Sensing strategy and Nanozyme mechanisms hypothesis

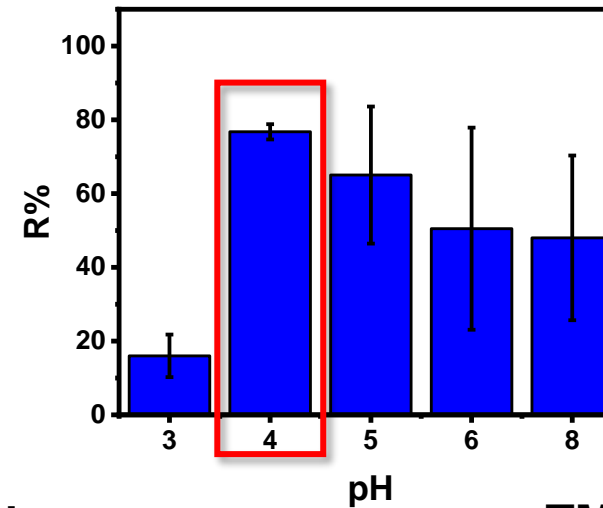


# LIM: Colorimetric determination of Ascorbic Acid

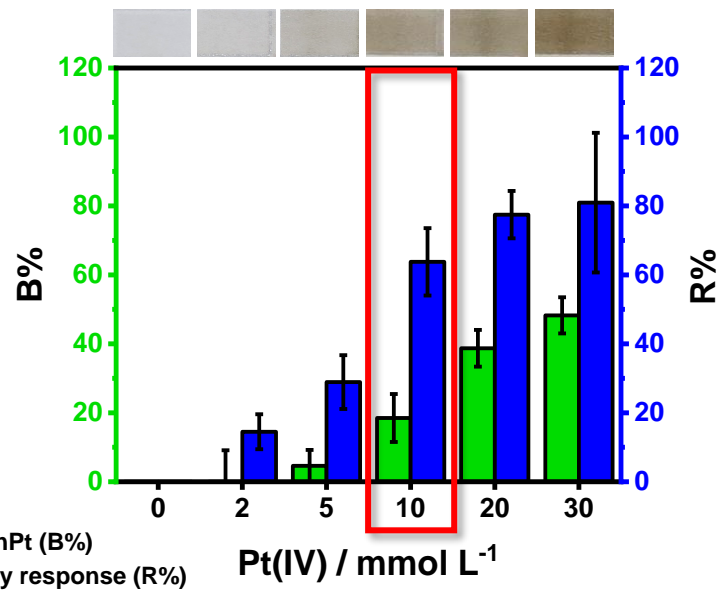
## Assay development



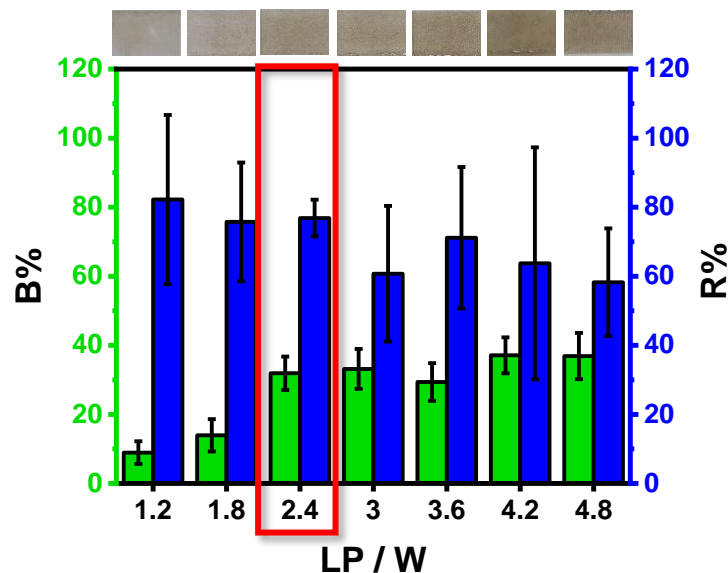
## Reaction conditions



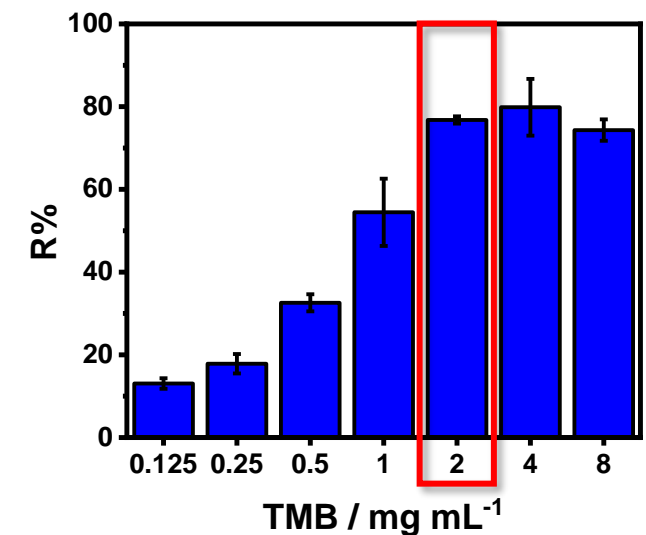
## Pt amount



## LIM-nPt synthesis



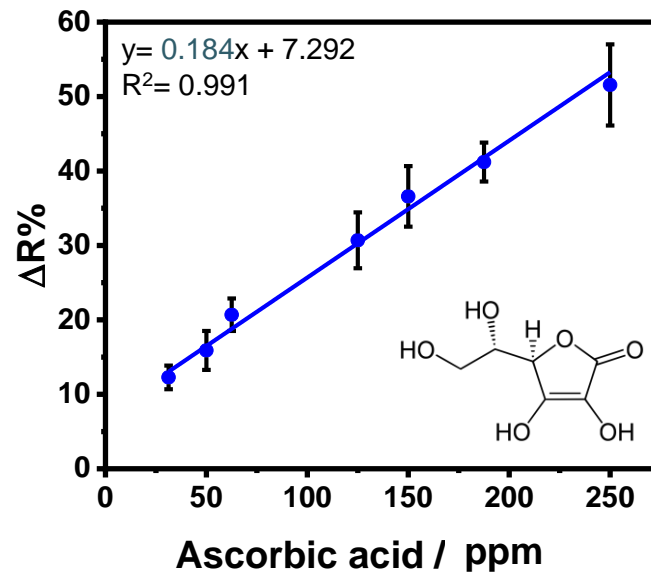
## TMB amount



# LIM: Colorimetric determination of Ascorbic Acid

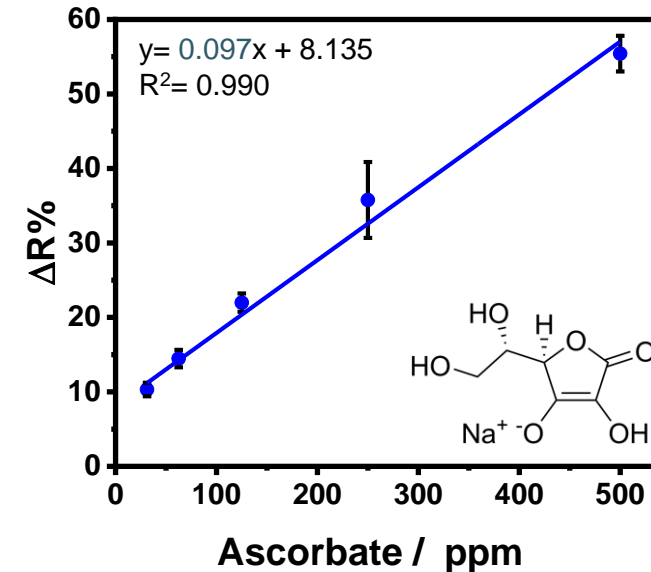
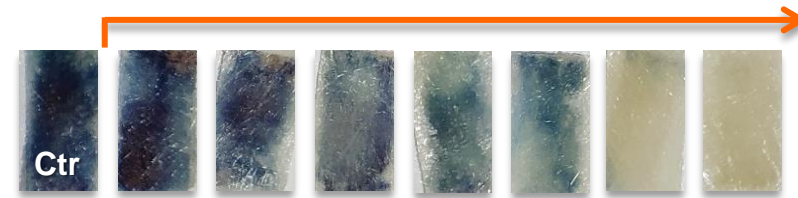
## Ascorbic acid determination

### L-Ascorbic acid (AA)



L.R.: 31- 250 ppm;  
LOD= 6.5 ppm  
RSD $\leq$  12%, n= 3

### Ascorbate



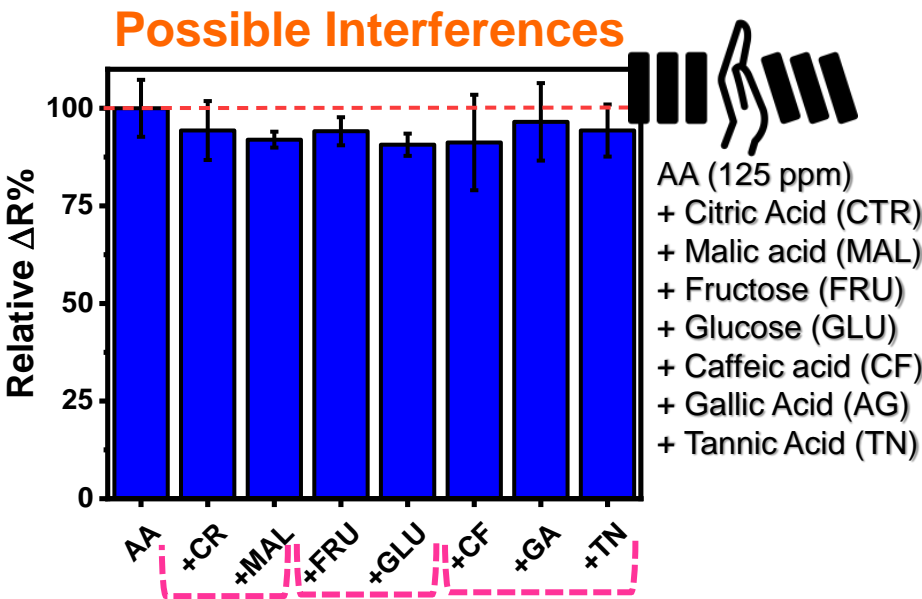
L.R.: 31- 500 ppm;  
LOD= 8.9 ppm  
RSD $\leq$  11%, n= 3





# LIM: Colorimetric determination of Ascorbic Acid

## Ascorbic acid determination in samples



	D.F.				D.F.		
	10	5	2		50	20	10
Lemon Juice-1				Rose hip			
Lemon Juice-2				Food supplier-1			
Orange Juice				Food supplier-2			
Organic Orange juice				Ctr			
Ananas juice							

Sample	Flip-PAD	std.dev.	Enzymatic Photom. kit	std.dev.	RELATIVE ERROR
	mg 100g <sup>-1</sup>		mg 100g <sup>-1</sup>		%
Lemon Juice-1	483.8	±32.6	545.3	±52.0	-11.3
Lemon Juice-2	1316.4	±48.9	1397.7	±98.9	-5.8
Orange Juice	24.6	±0.9	27.3	±2.0	-9.7
Organic Orange Juice	60.2	±2.0	60.1	±5.5	0.3
Ananas Juice	18.5	±1.3	18.6	±0.5	-0.5
Rose hip	55884.2	±1680.2	53574.3	±1562.8	4.3
Food Supplier-1	8689.2	±320.6	9530.2	±811.8	-8.8
Food Supplier-2	1291.3	±150.8	1329.9	±110.9	-2.9

**Recovery:**  
92 - 114 %  
RSD ≤ 7 %, n=3